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# ELECTROCHEMISTRY and ELECTROCHEMICAL ANALYSIS

A Theoretical and Practical Treatise  
for Students and Analysts

BY

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VOLUME II

GRAVIMETRIC ELECTROLYTIC ANALYSIS  
AND ELECTROLYTIC MARSH TESTS

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## PREFACE

The present book is published as Volume II of my Treatise on Electrochemistry and Electrochemical Analysis, the general scope of which is set out in the preface to Volume I. It has been found necessary to confine Volume II to the sections on Gravimetric Electrolytic Analysis, including Internal Electrolytic Analysis and Micro-chemical Methods, and to the Electrolytic Marsh Tests. It is hoped to publish the sections on Potentiometric and Conductimetric Titrations, Moisture Determination by means of Capacitance Measurement, and the Electrical Measurement of  $p_H$  as Volume III, when circumstances permit.

In the present volume particular attention has been devoted to the methods for separating metals by control of the cathode-potential with the aid of an auxiliary electrode. This method was considerably simplified by Lassieur more than ten years ago by the introduction of what may be described as high resistance voltmeters in place of the potentiometers previously used. When operated with the necessary precautions Lassieur's method is capable of yielding perfectly accurate results, by means which have now become even more simple owing to technical improvements in the apparatus required. Ten years ago Lassieur, basing himself on his experience as Deputy Chief Analyst of the Paris Municipal Laboratories, expressed the view that preference should be given to electrolytic methods of analysis for the examination of large numbers of industrial crude metals and alloys. It may be reasonably assumed that this view is justified even more widely at the present day than when it was first put forward.



Exhaustiveness has not been aimed at, and references to more specialized treatises and to original papers are made where necessary. I trust I shall be pardoned for having given perhaps undue prominence to those developments with which I have been personally associated.

It is hoped that the present volume will contribute to the more extensive employment of electrolytic methods, and that it will be found useful to students of practical and theoretical chemistry. In particular it is hoped that the brief explanatory characterization of each metal given in the chapter dealing with prescriptions for quantitative deposition will help to co-ordinate the practice of analysis with an appreciation of physico-chemical principles.

I have to record my thanks to Dr. A. J. Lindsey for compiling for me the list of references to papers on electrolytic micro-methods, to the authors and publishers of papers and manufacturers of apparatus for permission to reproduce illustrations and for the loan of blocks, and to Messrs. Gurney and Jackson for permission to reproduce some paragraphs from my article on Electrolytic Analysis in Lunge-Keane's *Technical Methods of Chemical Analysis*.

HENRY J. S. SAND.

LONDON, *January, 1940*

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## CHAPTER I

# APPARATUS FOR GRAVIMETRIC ELECTROLYTIC ANALYSIS

### Current Supply.

The usual source of supply is an accumulator battery. A six-volt medium-sized car battery should be sufficient for most purposes. Where A.C. mains are available charging by means of a battery charger is now a simple matter. Battery chargers consist of a transformer and a rectifier, and do not without an additional smoothing device give a current of uniform strength, but one that varies periodically from zero to a maximum with the variations in the primary alternating current. They are therefore in general unsuitable for direct application to electrolytic analysis. The rectifiers usually belong to one of two classes. Either they are "metal rectifiers" such as the Westinghouse copper-cuprous oxide rectifier, more fully described in Vol. III, or they are "valve rectifiers", such as the Ediswan "Tungar" rectifier, which consists essentially of a diode valve charged with a monatomic gas at low pressure, in practice argon.

If it should be desired to apply a battery charger direct to electrolytic analysis, this can be done by passing the current through a smoothing device consisting of a system of choke coils and condensers. Details of the construction of a smoothing outfit with a capacity of 1 ampere are given by A. J. Lindsey in a paper in the *Analyst*, 1938, 63, 425. For larger current outputs proportionally larger units may be employed.

Where only D.C. mains are available, battery charging is less simple and should be carried out by means of a small motor generator set. When only occasional electrolysis is contemplated, the D.C. mains may be connected to the ends

of a resistance consisting of lamps placed in parallel, and a suitable wire rheostat placed permanently in series with the lamps. The voltage required may be tapped from one of the ends of the wire rheostat and a slider belonging to it.

Of primary batteries only dry cells find a limited application in electrolytic analysis.

## Measuring and Detecting Instruments

### *Ammeters.*

For measuring current, dead-beat instruments should always be employed. An ammeter of the moving-coil type will usually be found most convenient. Such an instrument may be briefly described as a technical form of the well-known moving coil or d'Arsonval galvanometer, which has been placed on a suitable shunt.

### *Voltmeters.*

The voltmeters employed in electrolytic analysis are likewise usually technical forms of moving-coil galvanometers. These are placed in series with a high resistance, instead of being put on shunt with a low one, as are the ammeters. In recent developments of electrolytic analysis, viz. for the direct measurement of the P.D. between an auxiliary electrode and a cathode, a voltmeter taking only a minute current has become necessary. For this purpose a very suitable instrument in a technical form is available in the unipivot galvanometer of the Cambridge Instrument Company. In this a circular moving coil is mounted at its centre of gravity on a steel pivot in a powerful magnetic field, which is produced in a narrow gap between a spherical core and the pole pieces of a permanent magnet. The mode of construction, in which the pivot rests on a jewel bearing mounted on a spring at the centre of the spherical core, will be clear from figs. 1*a* and 1*b*. The advantage of this construction lies in the facts that great sensitivity can be easily obtained, that there is no necessity to level the instrument, and that vibrations hardly affect it.

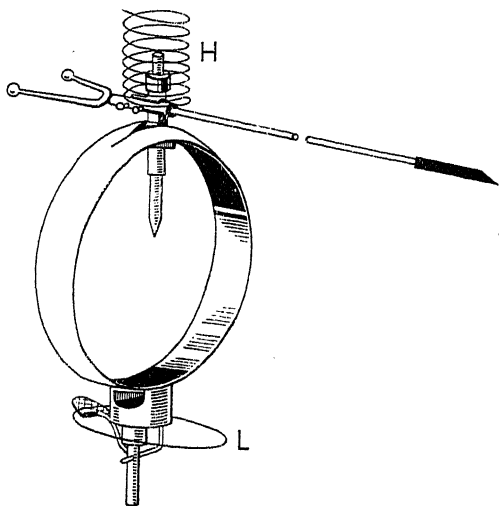


Fig. 1a.—Unipivot Voltmeter

The idea of a circular coil mounted at its centre of gravity was first exemplified by the "Onwood" galvanometer. For the application of the unipivot voltmeter to the measurement of cathode potential see p. 37. In place of the unipivot

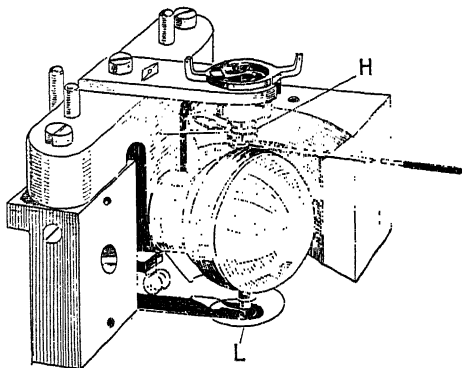


Fig. 1b.—Unipivot Voltmeter



voltmeter it is often possible to employ a simple pointer galvanometer which can be used in any position, the coil being suspended between two taut phosphorbronze strips. A wire resistance of about 50,000 ohms is placed in series with the instrument to make it suitable for use as a voltmeter.

### *The Lippmann Capillary Electrometer.*

Where only a zero instrument for P.D. is required, the Lippmann capillary electrometer may be employed. In this a capillary movable boundary between mercury and dilute

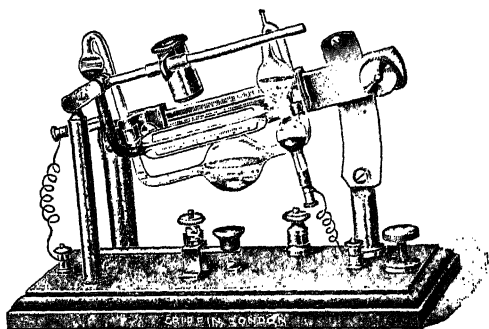


Fig. 2.—Capillary Electrometer

sulphuric acid is polarized either cathodically or anodically, when a P.D. is applied to the instrument. In the former case the surface tension of the mercury is increased, and the capillary boundary moves towards the body of the mercury; in the latter case the opposite effects occur. Repeated anodic polarizations cause the mercury meniscus to become fouled. The boundary in the capillary should then be renewed by the removal of a drop of mercury. The instrument must be kept short-circuited when not in use by means of a Morse key, so that polarizations may be discharged. A form of capillary electrometer, which is enclosed, was designed by S. W. J. Smith (*Phil. Mag.*, 1903, ser. 6, 5, 398). Modifications have subsequently been described by Luther (79th

meeting of deutsche Naturforscher und Aerzte), the author (*Trans. Faraday Soc.*, 1909, 5, 163) and G. F. Konowsky (*Zeit. Elektrochem.*, 1928, 34, 204). In all of these the sulphuric acid is freed from dissolved air and the instrument is evacuated. Fig. 2 illustrates the form used by the writer in his earlier work.

### *The Cathode Ray Detector.*

A detecting instrument which is likely to achieve much importance in the near future is the cathode ray or electron-beam tuning indicator, also known as the "electric eye" in

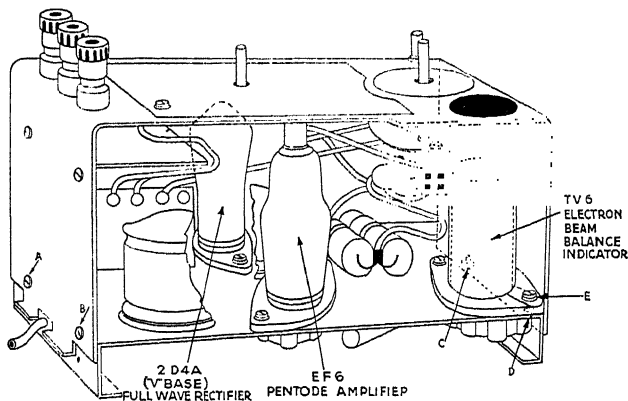


Fig. 3.—Measuring Bridge, showing the position of the valves and the balance indicator, and method of replacing

radio-technics. Used as a null instrument, the tuning indicator is suitable for detecting either continuous or alternating potential differences. As its sensitivity is insufficient for the purposes of electrolytic analysis, it is used in conjunction with a high-gain amplifying pentode valve, the combination being arranged for direct operation from the A.C. mains.

Sets are obtainable commercially in which all the apparatus required is supplied connected up in portable cases. For D.C. detection and proximate measurement a set has been

described under the name of the "Electron Beam Spectrometer" by G. F. Smith and V. R. Sullivan (*J.S.C.I.(T)*, 1937, 56, 104). For A.C. measurements the circuit is simpler owing to the possibility of employing "blocking condensers" where suitable. These transmit alternating, while they act as a barrier to continuous current. An assembly for the detection of alternating P.D.s which forms part of a Wheat-

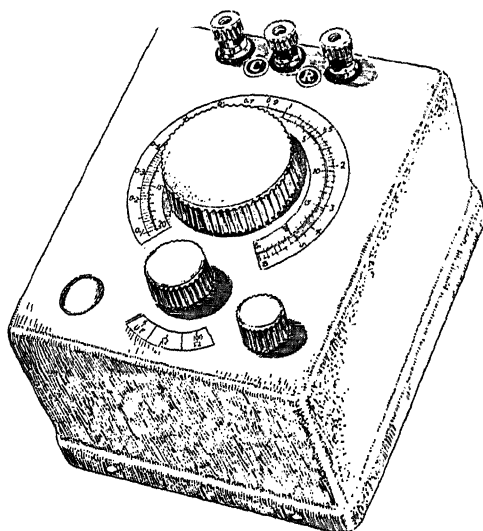


Fig. 3a.—Measuring Bridge, in case

Bridge" and the "Philoscop", "Type G.M. 4140". It is described by P. G. Cath in *Philips Technical Review*, 1937, 2, 270. We give an illustration of the instrument with cover removed and in its case in figs. 3 and 3a. It is designed for use with A.C. mains, but it may also be operated with a 6-volt battery, for which purpose a vibratory converter is supplied

(F.779)

by the makers. It is probable that an instrument of this type might also be used for detecting continuous P.D.s, if these were connected through a suitable interrupter such as the motor-driven micro-switch incorporated in the Marconi-Ekco  $p_H$  meter described in Vol. III. The bridge as supplied by the makers is arranged for the measurement of a wide range of resistances and capacities, a selector switch being incorporated which allows the operator to switch in the comparison standard required. Fig. 4 shows the fundamental circuit.

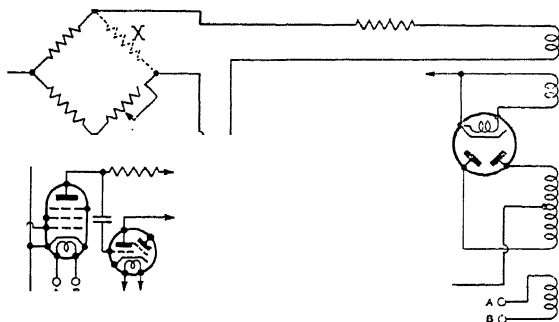


Fig. 4.—Fundamental Circuit of the G.M. 4140

We give a detailed description only of the indicator itself. Essentially it consists of a miniature cathode-ray tube mounted above a triode valve, the two having a common vertical cathode, and forming a single unit. Fig. 5 gives a diagrammatic illustration. C is the common cathode which is indirectly heated, the heating wires being omitted in the diagram. At the top of the cathode there is a shield S for screening off the light proceeding from it, so that a dark central disc is perceived on looking down into the instrument. G is the grid, and P the anode or plate of the triode. T is a conical frustum, which forms the anode or target of the cathode-ray tube. Whereas the latter is connected directly to the positive end of the source of supply of 200 to 300 volts, the plate of the triode is connected through a resistance

$R$  of one or more megohms. The target  $T$  is coated with a substance that fluoresces under the impact of the cathode rays, and can be observed on looking down from the top of the tube. Protruding into the field of the cathode rays are one or more vertical wires or control electrodes  $W$  which are attached to the plate  $P$  of the triode. It will be seen that the potential of these wires is negative to that of the target by an amount equal to the resistance  $R$  multiplied by the current  $I$  flowing through the triode. This current is controlled by

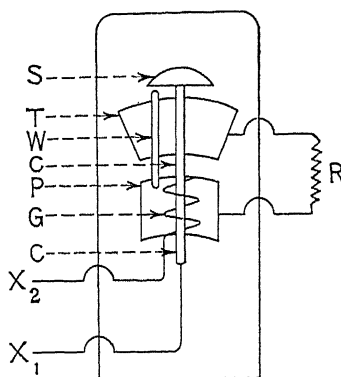


Fig. 5.—Tuning Indicator

the P.D.  $X_2 - X_1$  between the grid and the cathode. When it increases, the control electrodes  $W$  therefore become more negative, and repel electrons, thus throwing a well-defined shadow on the target  $T$ , which is visible whether the increase is continuous or not. With most indicator tubes a grid bias  $X_2 - X_1$  of  $-5$  to  $-8$  volts causes the shadow practically to disappear, whereas with zero grid bias it fills the whole of the tube. The apparatus can thus be arranged to detect potential differences. In the "Sectrometer" a bias is put on the grid, just sufficient to cause the original P.D. to produce a minimum shadow. A variation of amplification by the pentode is obtained by means of two ganged resistances and

## GRAVIMETRIC ELECTROLYTIC ANALYSIS

fine adjustment of the shadow is obtained by controlling the grid bias of the pentode.

In the "Mullard Bridge" four wires *W* are employed, so that a luminous cross is visible, which is at a minimum for zero P.D. Sensitivity is controlled by variation of the grid leak of the tuning indicator.

The use of the tuning indicator as a bridge detector was suggested almost simultaneously by M. Breazeale (*Rev. Sci. Instr.*, 1936, 7, 250) and by D. Ulrey (*Physics*, 1936, 7, 97).

### Potentiometers.

Where, as in gravimetric electrolytic analysis, a potentiometer is required for occasional use, and a result that can be relied upon to within a centivolt is sufficient, the circuit is

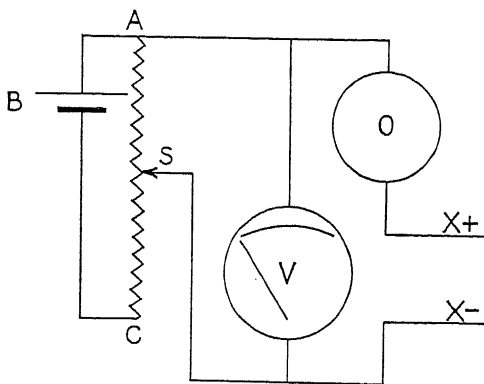


Fig. 6.—Tafel's Potentiometer Circuit

usually employed which was used by J. Tafel in his researches on polarization (*Z. Phys. Chem.*, 1905, 50, 662). In it, as is shown in fig. 6, the terminals of a cell *B* are connected to the two ends of the sliding rheostat *AC*. Thus any voltage between zero and that of the cell may be tapped off between *A* and the slider *S*. The latter is moved until this variable voltage just balances the voltage to be measured

between the two points indicated as X+ and X—. The balance is detected by a null-point indicator instrument shown as O, and the value of the voltage is read directly on a voltmeter V placed in parallel to AS. Details of a potentiometer assembly based on Tafel's circuit, in which, however, a uni-pivot voltmeter plays the part both of the null-point and of the measuring instrument, and in which it may also be connected directly to the two points under measurement, are given on p. 38. Potentiometers are further discussed in the section on  $p_H$  measurement of Vol. III.

## Electrodes and Stands

### *Material and Form of Electrodes.*

The anode must be of inert metal, and it is doubtful whether any satisfactory substitute for platinum has been found. The amount of this need not be great, as the metal can be used as thin gauze, the weave being normally smaller than that of the cathode. It may be mounted on a glass frame. For the construction of the cathode, platinum is likewise the most important material, and the ease with which metal deposits may be stripped from it make it more generally applicable than any other substance. However, for many determinations cathodes of silver, nickel, brass or mercury may be employed. The cathode should be of a nobler metal than the one to be deposited. Thus silver electrodes may be used for copper and some other determinations. For the removal of copper, cadmium, or zinc H. W. Doughty and B. Freeman (*J. Amer. Chem. Soc.*, 1921, 43, 700) have proposed a cold solution containing 20 gm. trichloroacetic acid, 100 millilitres ammonia, sp. gr. 0.900, and 100 millilitres water. A previous suggestion by the writer was the employment of hot dilute sulphuric acid (1:10) to which some hydrogen peroxide free from chlorides ( $2\frac{1}{2}$  millilitres perhydrol per 100 millilitres) has been added. In all cases in which acid stripping agents for silver cathodes are employed,

it is advisable to wash them also in a bath of dilute ammonia, in order to avoid any possibility of sparingly soluble silver salts remaining, which would later be reduced, and falsify the results completely. If a silver electrode appears black through roughening after use, or has become stained by sulphide, it may be brought back to its original condition by ignition to a dull red heat. Care must be exercised in this operation, in order to avoid melting of the silver.

The use of mercury as a cathode offers advantages in two directions. First, owing to the fact that most metals dissolve in mercury, there is no difficulty in obtaining them in a coherent form, secondly, owing to the low deposition energy of metals in mercury, and its high hydrogen overvoltage, it is possible to utilize mercury cathodes for many determinations, which are impossible with solid cathodes. On the other hand, mercury cathodes are not readily adaptable for effecting separations, and the volatility of the metal is a source of difficulty. For a discussion on the use of mercury cathodes the reader is referred to a paper by W. Böttger and collaborators (*Zeit. Anal. Chem.*, 1933, **93**, 401), in which further references will be found.

In the hands of E. F. Smith and his collaborators the use of mercury cathodes has considerably extended electrical methods of chemical analysis. Thus fig. 7 shows a cell designed by J. H. Hildebrand (*J. Amer. Chem. Soc.*, 1907, **29**, 447), in which anions forming insoluble salts and cations such as sodium may be determined simultaneously. In principle it resembles the Castner Kellner cell for the manufacture of caustic soda. The apparatus comprises an outer cell consisting of a crystallizing dish 11 cm. in diameter and 5 cm. deep. Inside this is a beaker 6 cm. in diameter, the bottom of which has been cut off, so that a ring is formed 4.5 cm. high. This rests on a triangle of thin glass rod on the bottom of the crystallizing dish, and is kept in position by three rubber stoppers as shown. The object of this ring is to allow the inner compartment to be hermetically sealed from the outer by means of mercury. A film of solution, however, was found to form between the glass and the mercury, permitting a



small quantity of the salt to diffuse from the inner to the outer compartment. To prevent this the lower rim of the bottomless beaker was first platinized and then silver-plated to a width of about 4 mm. This was effected by the use of a saturated solution of chloroplatinic acid, to which an equal volume of glycerin was added; this solution was painted on the bottom rim of the ring, the latter dried at  $300^{\circ}$ , and

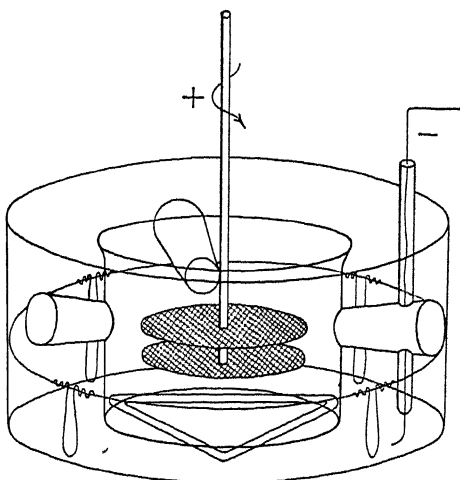


Fig. 7.—Hildebrand's Cell

afterwards carefully heated in a bunsen flame till the glass just began to soften. The film of adherent platinum was then made the cathode in an agitated solution of potassium silver cyanide, and a heavy layer of silver deposited on it which was finally amalgamated by contact with mercury. In the outer compartment there is a spiral of about six turns of nickel wire, supported about 1 cm. above the surface of the mercury by wire legs.

The anode consists of two circular discs of platinum gauze, each 5 cm. in diameter, of mesh 45 per linear inch. These are mounted 5 mm. apart on a 1 mm. platinum stem, to

which a hook of platinum wire is fitted about 2 cm. from the top for suspension to the balance. For the determination of anions forming insoluble silver salts these electrodes are coated with 3 to 4 gm. of silver from a cyanide plating bath. Anions such as  $\text{Cl}^-$  or  $\text{CNS}^-$  are then retained as insoluble salts on electrolysis, and may be weighed. Several determinations can be made without replating the gauze, the deposited silver salt being merely dissolved off by immersing for a few moments in potassium cyanide solution, and thus exposing a new silver surface. For the estimation of sulphur in sodium sulphide, the anode is plated with cadmium instead of silver.

In using the cell, which must be kept scrupulously clean, pure mercury is poured in, so that its level is about 3 mm. above the lower edge of the bottomless beaker. The anode is fitted about 5 mm. above the surface of the mercury, and may be left stationary, but is preferably rotated at about 300 revolutions per minute. The current is led out of the cell from the mercury. The solution to be electrolysed is put into the inner compartment; sufficient distilled water to cover the nickel wire is placed in the outer compartment, and to this is added 1 millilitre of a saturated solution of common salt. By this arrangement the amalgam formed in the inner compartment is decomposed as soon as it comes into the outer division, the latter acting as a short-circuited galvanic cell, the plates of which are the amalgam of the metal deposited and nickel respectively, and the electrolyte, sodium chloride. The sodium hydroxide formed in the outer compartment is determined by titration. Quantities of salt up to about 0.1 gm. were electrolysed in this apparatus with current strengths up to a little over  $\frac{1}{2}$  amp. in times varying between about half an hour and an hour.

When, as was shown by McCutcheon and Lukens of Edgar F. Smith's laboratory (1907), neutral solutions of metals forming insoluble hydroxides are placed in the inner compartment of the apparatus, the metal is not deposited as an amalgam, but instead, hydrogen and hydroxide are formed. Metals belonging to this class are aluminium, magnesium,

uranium, chromium, iron, manganese, cadmium, tin, and others. Calcium is on the boundary line between those metals, which remain as insoluble hydroxides in the inner compartment, and those which first form amalgams, and then find their way as soluble hydroxides into the outer. Hence it comes about that when low voltages up to about 3 are applied to the apparatus, calcium remains in the inner compartment,

but when higher voltages of about 9 are employed, it passes into the outer. It is clear that the facts described may be employed to effect the separation of metals migrating to the outer compartment from those remaining in the inner.

For the precipitation into mercury cathodes, of metals such as copper, bismuth or zinc, which are also deposited from aqueous solution on metals other than mercury, the arrangement may be employed which was elaborated by W. M. Howard, and is shown in fig. 8 (E. F. Smith, *Electroanalysis*, p. 66, Philadelphia, 1918). It consists of a small beaker of about 50 millilitres capacity, through the side of which near

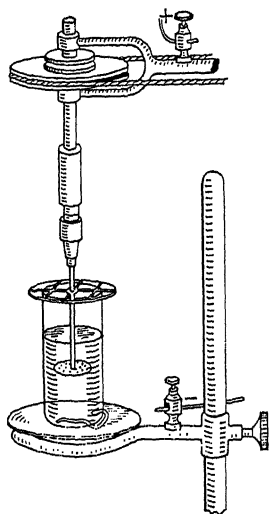


Fig. 8.—Mercury Cathode:  
Howard's Arrangement

the bottom a thin platinum wire is introduced. Internally the latter dips into the mercury, while externally it is bent under the beaker, so that, when the latter is placed on the disc of metal shown, electrical connexion to the source of current is made. After a determination the solution in the beaker is replaced by water in the manner described on p. 48, the walls being well rinsed. The water is then poured into a dish, leaving the mercury behind. This operation is repeated with alcohol and finally with ether, or with two washings of acetone. The ether or acetone is evaporated in a jet of cold

air, obtained from a hand bellows, the outside of the beaker is wiped with a cloth, and after standing for fifteen minutes is weighed with its contents.

More recently H. Paweck and his co-workers (*Z. Anal. Chem.*, 1927, **72**, 225, *ibid.* 1929, **79**, 115; see also H. A. J. Pieters, *Chem. Weekblad*, 1928, **25**, 706) have advocated the use of cathodes of Wood's metal or other fusible alloy. These alloys are employed in the liquid state during deposition, but are weighed in the solid state. They have most of the advantages of mercury for cathodes, and there is no difficulty in drying arising from the volatility of the metal. Like mercury they do not, however, lend themselves to separations.

Amalgamated metals have some of the advantages of mercury as a material for electrodes, and are sometimes employed in the deposition of silver (p. 54) and of zinc (p. 80).

In the older work on electrodeposition for analysis, cathodes made from foil were employed. In 1898 H. Paweck (*Z. Elektrochem.*, 1898, **5**, 221) introduced wire gauze cathodes of amalgamated brass, which were followed in 1899 by platinum gauze cathodes, introduced by Cl. Winkler (*Ber.*, 1899, **32**, 2192). Since then most cathodes have been constructed of gauze. Such electrodes offer the advantage of good permeability to the electrolyte, and therefore of good circulation. Further, the deposit is spread fairly uniformly on both sides of the electrode, and tends to adhere well. The mesh should not be too fine if washing is not to be made difficult, and on no account may solid particles be present in the electrolyte, unless they are dissolved completely during the course of the electrolysis.

In all the older work stationary electrodes were employed. Artificial stirring was first suggested by v. Klobukow in 1886 (*J. Prakt. Chem.*, 1886, **33**, 473). Whether the latter is employed or not, circulation of the liquid, promoted either by gases produced during electrolysis or by suitable heating of the electrolyte, is a factor of first-rate importance in determining the efficiency of the electrodes.

*Stationary Electrodes.*

Fig. 9 represents the "Luckow", one of the earliest types of electrodes. It will be noticed that the cathode is a cylindrical piece of foil, whereas the wire anode is arranged in such a way that the gas bubbles liberated from it at the bottom of the beaker stir the whole of the electrolyte. The cathode was later modified to the form of a truncated cone and slits were sometimes introduced into it to promote circulation of the electrolyte.

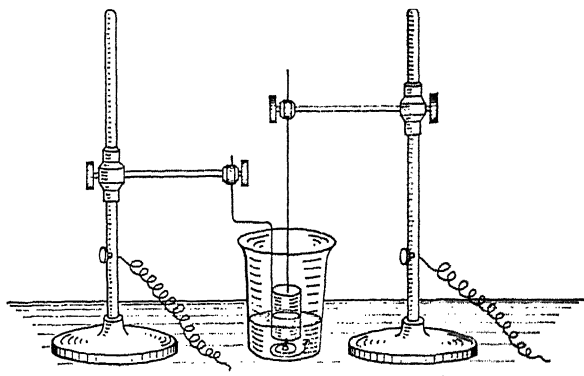


Fig. 9.—Luckow Electrode

Figs. 10a and 10b illustrate the platinum dish, the employment of which was popularized by A. Classen, and the stand, fitted with a glass insulating rod that was used with it. Figs. 11a, 11b and 11c represent anodes. The dish was sometimes roughened by sand-blasting to increase the adherence of deposits, but such roughening according to O. Scheen (*Z. Elektrochem*, 1908, 14, 257) promotes the inclusion of impurities. This difficulty is met according to Classen by roughening the dishes only very slightly by dilute aqua regia. The main objections to the dish are the very large amount of platinum required, and the poor circulation of the liquid. The latter objection can be very largely met by heating the

dish gently during electrolysis. For this purpose a piece of sheet asbestos may be attached to the ring supporting the dish, and a bunsen burner is placed underneath. The anode may also be rotated mechanically, when the dish becomes one of the most efficient forms of apparatus for rapid deposition (Julia Langness, *J. Amer. Chem. Soc.*, 1907, 29, 460).

Fig. 12 illustrates the gauze cathode and wire anode due to

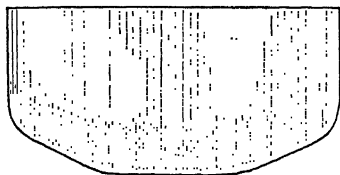


Fig. 10a

Platinum Dish and Stand (Classen)

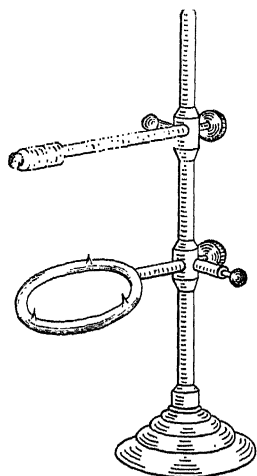


Fig. 10b

Hollard (A. Hollard and L. Bertiaux, *Analyse par Electrolyse*, Paris, 1906, p. 11). The latter is arranged to transmit

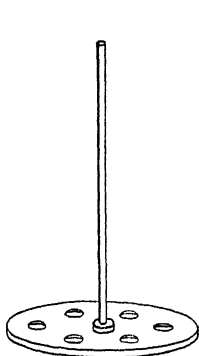


Fig. 11a

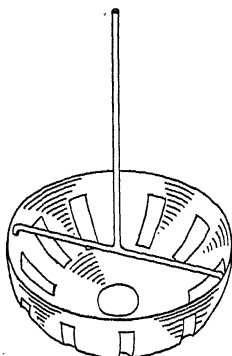
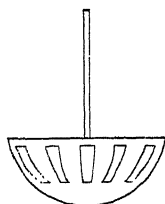
Fig. 11b  
Anodes

Fig. 11c

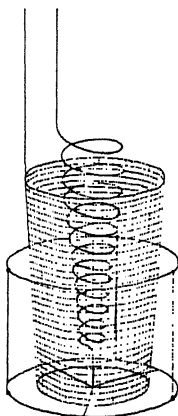


Fig. 12.—Hollard's Gauze Cathode and Wire Anode.

current to the cathode both from inside and from outside. Most analysts will probably prefer a simpler anode, which is confined to the interior of the cathode.

Reference should here be made to papers by Gooch and his co-workers, in which devices are described, by means of which the electrolyte is filtered through asbestos felt either continuously during electrolysis or at the end of an operation. By this means the necessity of securing adherent deposits on the cathode is avoided (*Amer. Journ. Sci.*, 1908, [4], 34, 107; *ibid.* 1914, [4], 34, 107; *ibid.* 1917, [4], 43, 391).

### Apparatus Designed for Vigorous Stirring of the Electrolyte

The very great importance of vigorous stirring of the electrolyte has already been discussed (Vol. I, p. 127). About 1903 it was shown independently in the laboratories of E. F. Smith in Philadelphia, F. A. Gooch in Yale, and A. Classen in Aachen, that copper determinations, which by previous methods required times varying from two hours upwards, could be carried out in from ten to twenty minutes, if only the electrolyte was stirred vigorously. In 1907 the apparatus designed by the writer, which we believe to be more generally adaptable than other forms, was described. Before discussing the latter, we shall give a general survey of other forms, each of which has its own advantages.

F. A. Gooch and H. E. Medway rotated a cathode consisting of a platinum crucible of about 20 ml. capacity, suitably closed by a rubber stopper, at 600 to 800 revolutions per minute, at the same time employing considerably higher

current densities than had been previously used. The anode was a piece of foil or wire of suitable form. Amberg in the Aachen, and Exner in the Philadelphia laboratory employed dishes as cathodes, the stirring being effected by anodes of one of the forms shown in figs. 11*a*, 11*b* and 11*c*.

Purely electromagnetic stirring, without the use of mechanical devices, is attained in the ingenious apparatus due to F. C. Frary, shown in fig. 13 (*J. Amer. Chem. Soc.*, 1907, 29, 1592; *Z. Elektrochem.*, 1907, 13, 308). Here the current passes through the electrolyte radially between a central anode and an outer gauze cathode. It also passes through a solenoid, which surrounds the electrolytic vessel, so that the vertical magnetic lines intersect the horizontal lines of flow of the current in the beaker at right angles. The result is, that when a sufficiently large current is employed, rotation of the liquid is produced. Frary also designed an apparatus for use with a mercury cathode, in which the lines of flow of the current in the beaker are vertical, and the magnetic lines horizontal and radial. In apparatus of this class the current can obviously not be reduced without also diminishing the rotation of the electrolyte, and in other respects as well it is not very adaptable.

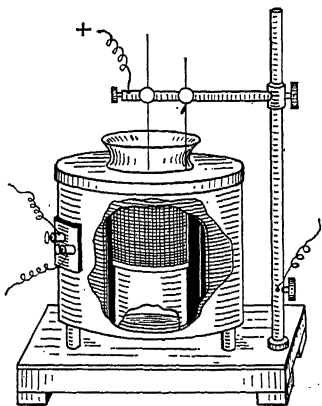


Fig. 13.—Electromagnetic Stirring (Frary)

The same objection generally applies to apparatus in which gases liberated at the electrodes are relied upon to produce the necessary circulation of the electrolyte. Externally generated gases are, however, sometimes usefully employed. Thus F. Fischer, C. Thiele and E. Stecher (*Z. Elektrochem.*, 1911, 17, 905) used hydrogen taken from a cylinder through a



reducing valve. Another suggestion due to the same experimenters was to keep the electrolyte boiling under diminished pressure. The effect of the diminished pressure is not only to cause the liquid to boil at a lower temperature, but also to increase the size of the gas bubbles, so that the efficiency of stirring is greatly enhanced. The vessel was a large boiling tube. When the electrodes are placed at the bottom, there is no trouble from bumping. The vacuum is obtained from an ordinary laboratory water-injector air-pump.

### Electrodes Designed for Use with an Auxiliary Electrode

*The Writer's Electrolysis Apparatus.—Fischer's Electrodes.—Lassieur's Electrodes.*

The distinguishing features of the writer's electrodes are an outer stationary gauze electrode for receiving the deposit and an inner gauze electrode which acts as a stirrer. The electrodes are designed so as to confine the lines of flow of the current between them, so that, when a connexion to an auxiliary electrode is placed anywhere in the liquid outside the outer electrode, the P.D. between the former and the latter depends practically only on the P.D. between the outer electrode and the electrolyte, being independent of the other electrode and of the P.D. expended on forcing the current through the liquid. The stem of the inner electrode rotates in a glass tube, which is held by a clamp, that also makes connexion to the outer electrode. Connexion to the inner electrode is made by a clutch, fitted to a flexible drive, usually consisting of a rubber tube filled with mercury. The support for the beaker is always made readily removable from underneath, so as to facilitate disconnecting.

*The Original Electrodes.*

Fig. 14 shows the original electrodes (*Trans. Chem. Soc.*, 1907, **91**, 373; *Trans. Faraday Soc.*, 1909, **5**, 159). The

outer electrode is bell-shaped and surrounds the inner everywhere except from below. The glass tube is slipped through the collar and ring of the outer electrode, and the stem of the inner is pushed up through it, after which the pair is ready for connexion to the stand. Obviously the pair can be carried safely by means of the stem of the inner, but not by means of the outer electrode, a fact that is sometimes overlooked, and may then lead to damage to the inner electrode. The latter has a central vertical plate, in order to produce maximum rotation inside. This rotation is stopped by the outer electrode, so that the liquid is thrown out from the centre of the outer electrode by centrifugal force, and suction takes place at the top and the bottom, good circulation being produced. The objection may be urged against these electrodes, that they require a large weight of platinum amounting to about 2 oz. Also the outer electrode does not lend itself readily to the removal of a deposit by a small amount of solvent. This is required, when two metals have to be deposited together first and to be separated subsequently, after having been again brought into solution. For efficiency of stirring and rapidity and smoothness of work these electrodes are, however, probably superior to the others that have been described.

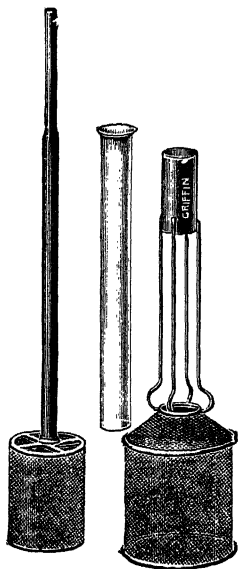


Fig. 14.—The Original Electrodes

#### *Modified Electrodes.*

To meet the objections mentioned, the assembly of electrodes and tripod, depicted in figs. 15*a*, *b* and *c*, has been designed (*Analyst*, 1934, 59, 335). Here the gauze of the

inner electrode is mounted on a pipette-shaped flat-bottomed glass frame. The edges of the foil are stiffened by foil and held in position on the frame by two rows of eight beads each, at a distance of about 2 mm. from the body of the frame, so that large bubbles of gas, which tend to move inwards during rotation, may have an opportunity to escape.

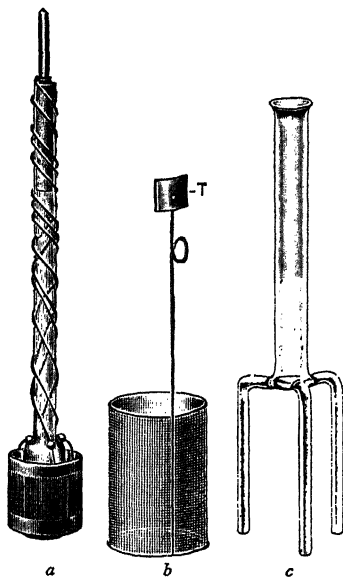


Fig. 15.—Modified Electrodes

The connexion to the revolving clutch is made by a silver peg of about  $3\frac{1}{2}$  mm. diameter. In the older construction shown in the figure, which lends itself to the use of quartz glass, the silver peg was cemented into the tube by molten lead, which had been freed from oxide by running it into position in the liquid state. The connexion to the platinum cylinder was made by platinum wires wound round the stem. Owing to the fact that the lead adhering to the glass sometimes caused the latter to crack, this construction has

been replaced by one in which the peg is keyed into the frame by solder. The method is explained by fig. 16. A glass tube is chosen for the stem into which the silver peg just fits. It is constricted to an elliptical cross-section below the peg, so that a small piece of solder placed on the other side of the constriction can be melted to run through the constriction and form a joint with the peg, which is thus keyed into the tube. The stem and solder are carefully annealed. A cross-section of the stem at the constriction is shown at *s*. A stout copper wire is connected to the solder, and connexion is made from the bottom of the wire to the gauze of the electrode by means of platinum wires or gauze sealed into the frame. The copper wire is hindered from vibrating in the stem by means of a little asbestos fibre pushed in at the bottom. To prevent the stem from chafing its guide-tube a platinum wire of about 0.1 mm. is soldered to the silver peg, wound spirally round the stem, and is caught, i.e. lightly fused on the glass below. The gauze cylinder is also caught on the glass beads. The diameter of the gauze jacket of the inner electrode is about 2.5 cm. and its height also about 2.5 cm.



Fig. 16.—Peg with solder

The outer electrode shown in fig. 15*b* is made in the form of a cylinder of 3.2 mm. diameter and 5 cm. height. It is found that when the inner electrode is adjusted to about half as far or slightly less from the bottom as from the top of the outer one, the lines of flow of the current are confined sufficiently between the electrodes, and that good stirring results. In order that the outer electrode may be light and yet rigid the glass tube of the original pattern has been developed into a tripod, the legs of which hold the electrode in position. The leading-in wire of the latter is made of 0.8 mm. wire. This is welded to the bottom of the electrode cylinder and attached loosely by a wire loop at the top, a method of construction that ensures enough "give" to prevent the wire breaking from bending or from vibration. The wire goes up vertically for a distance equal at least to the length of the

cylinder, and is then bent inwards through a loop towards the guide-tube, where it ends in the tab 'T' for connexion to the silver-lined clamp described below. The tab may be omitted if the wire is bent at its end to an angle with the axis of the guide-tube.

The tripod is shown in fig. 15c. If one of its legs is accidentally broken, and has to be repaired, it is obviously necessary to ensure that its distance from the axis of the guide-tube should be accurately equal to the radius of the electrode cylinder.



Fig. 17.—Template for Tripod Leg

This can be easily attained if use is made of the template shown in fig. 17. This consists of a tube or rod which can be pushed into the guide-tube, into which it fits accurately. The position of the tip, determined by the length  $a$ , which is equal to the radius of the electrode cylinder, serves as a guide in fixing the leg correctly. The design of the assembly described makes it possible, after loosening the clamp for disconnecting, to pull the outer electrode down out of the tripod without taking off the latter and the inner electrode. The weight of the platinum outer electrode is between 9 and 10 gm. Electrode

assemblies of the kind described are manufactured by Messrs. Griffin & Tatlock of Kemble Street, Kingsway, W.C.2.

### *Cathodes of Silver, Brass or Nickel.*

Outer electrodes of the same general type as the one illustrated in fig. 15b may be readily improvised from gauze of silver, brass or nickel. Such electrodes may be tied together by wire; in the case of silver, however, joints are best made by welding. This process is carried out just as with platinum by heating the parts to be joined a short distance above an anvil, and then performing the weld by means of a sharp blow from a hammer. To avoid melting of the silver care must be taken to heat it only to a dull red heat. The leading-in wire of fig. 15b is replaced by a strip of gauze or of foil, which is provided with a hole for suspension to the balance. It is

often found advisable to construct such electrodes of a diameter sufficient to allow them to be held outside instead of inside the legs of the tripod; a larger deposition surface and a more uniform distribution of the current are thus assured. Silver electrodes are used with great advantage in the deposition of copper, amalgamated brass electrodes in the deposition of zinc, see p. 80. For the treatment of silver electrodes and the removal from them of metal deposits, see p. 10.

### *Rubber-frame Electrode.*

Fig. 18 is designed to explain an anode that may be improvised in the laboratory. It has been found useful in carrying out determinations at ordinary temperature, and is distinguished by great resilience. A piece of thick-walled rubber tubing free from metal oxides is slipped over the stem of the electrode. On this are clipped eight glass hooks, two of which are shown. These support the jacket of platinum gauze, which may be further held in position by platinum wire. Four platinum wires sealed through the stem make connexion to the leading-in peg.



Fig. 18.—Improvised Electrode

### *Diaphragm Electrode.*

The electrode to be described is designed to be used as an inner electrode in conjunction with a diaphragm, when oxidation or reduction of the test electrolyte must be avoided. Thus in the deposition of copper from a solution containing a high concentration of iron salts, it is necessary that the iron should be maintained in the ferrous condition, since ferric salts dissolve copper, and it is found with ordinary electrodes that the current may under unfavourable circumstances be used up exclusively as a "residual" current (Vol. I) in causing alternate oxidation and reduction between the ferrous and ferric states. Such a result may be avoided by placing the anode in an indifferent electrolyte in a separate compartment. Similarly in the separation of cobalt from nickel by deposition as cobaltic

oxide on the anode, it is necessary to place the cathode in a special compartment in order to prevent deposition of metal. The diaphragm electrode is explained by the sectional drawing (fig. 19) and the view (fig. 19a). The electrode is made to carry a parchment thimble, which revolves with it, and holds an auxiliary electrolyte, say a dilute acid or a salt solution. The thimble is cut from a Whatman diffusion shell of 16 mm. diameter to the correct length, and provided with one or two vertical slots at the top. It is then thoroughly

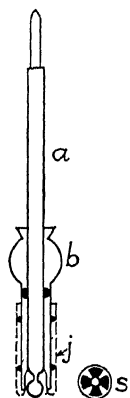


Fig. 19.—Diaphragm Electrode

soaked in water, slipped over the electrode, and fastened to the funnel-shaped portion by means of thread. Since a small amount of the ions to be determined will diffuse through the parchment, the electrode is designed so that the whole of the liquid contained in the chamber formed by it may be washed outside at the end of a determination and be displaced by fresh liquid. For this purpose the electrode is constructed of an inner tube *a*, holding a silver or aluminium leading-in rod, to which four platinum



Fig. 19a.—Diaphragm Electrode

To the bottom of the tube *a* is fused a protrusion carrying four arms to which the outer tube *b* with a funnel top is sealed. The bottom of the electrode thus presents the appearance of having four holes, as shown by *s*. Alternatively the inner and outer tubes may be joined directly by an inner seal, the bottom being slightly expanded and four holes blown in it, as shown in fig. 19a. The tube *a* carries four beads of such a size as to keep the tube *b* in position, and thus strengthen the electrode, whereas the tube *b* carries two rows of eight beads for holding the platinum jacket *j*. The leading-in wires are sealed into tube *a*, taken through the holes at the bottom

of the electrode, and fastened to short wires welded to the platinum jacket *j*. This electrode is used with a tripod having slightly longer legs than those employed with the ordinary inner electrodes.

#### *A. Fischer's Electrodes.*

As already stated, the writer's original electrodes require a somewhat high weight of platinum. To avoid this A. Fischer (*Z. Elektrochem.*, 1907, 13, 469) used a pair of stationary

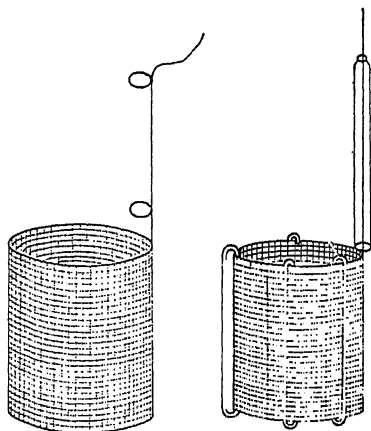


Fig. 20.—Fischer's Electrodes

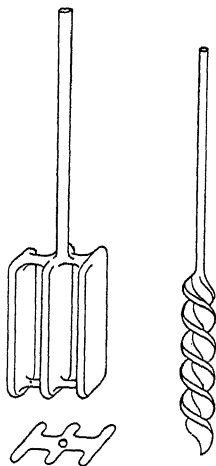


Fig. 21.—Stirrers

concentric gauze electrodes with an external stirrer, the general effect being the same as with the writer's electrodes. As with the latter, the members of the pair are held rigidly in their relative positions. This is attained, as shown in fig. 20, by fitting around the inner electrode a number of glass rods of about  $3\frac{1}{2}$  mm. diameter, which are bent over its edges. The stem holds a glass tube which serves as a support to two platinum loops fitted on the stem of the outer electrode, resting on some beads fused to the tube. Fig. 21 represents stirrers used with these electrodes.



*Lassieur's Electrodes.*

Lassieur's electrodes were designed to serve the same purpose as those of the writer and of Fischer. They comprise a platinum gauze outer stationary electrode of 5 cm. diameter and 5 cm. height, and an inner stirrer electrode, consisting of an H-shaped glass frame, on which platinum wire of 0.3 mm. thickness is wound.

*Mesh of Wire Gauze.*—As already stated, the wear on the gauze of the inner electrode, on which usually only gases are liberated, is slight, and it is possible to employ gauze of a wire thickness down to about 0.075 mm. and having a mesh of say 80 per linear inch, or about 30 per linear centimetre. On the other hand, it is not advisable to allow the wires on the outer electrode to have a smaller thickness than 0.15 mm., and a greater diameter is preferable. Such gauze usually has a mesh of about 45 per linear inch, or say 17 per linear centimetre. W. D. Treadwell (*Elektroanalytische Methoden*, p. 42) estimates that gauze of 0.2 mm. wire and a mesh of about 15 per linear centimetre has an effective surface equal to about twice the plane area covered by the gauze. With the usual sizes of gauze having thinner wires the effective area is somewhat smaller.

### Electrical Connexions and Stands for Work with Controlled Electrode Potentials

Fig. 22 shows the wiring diagram employed by the writer. It will be seen that provision is made for regulating the current by a sliding rheostat, which may be of about 3 ohms resistance and 15 amp. carrying capacity. When simple depositions are made, the shunt switch SH may be left open. The working electrodes are then in series with the rheostat. When, however, the shunt switch is closed, the whole voltage of the battery is placed on the terminals of the rheostat, and by moving the slider, the P.D. applied to the electrodes may be varied continuously between 0 and the voltage of the

battery. The reversing switch RS allows either electrode to be used as cathode or as anode. The central terminal P is utilized when the stand is employed for potentiometric titrations, as will be explained in Vol. III. The current is read on the ammeter A, which should have a range of 0 to 10 amp. The voltmeter V, which may have a range of  $-10$  to  $+10$  volts, is useful for indicating the direction of the applied P.D. and the power consumption across the electrodes, but may be omitted.

Distinctive features of the writer's stands are a flexible drive with special chuck for the inner electrode, a permanent

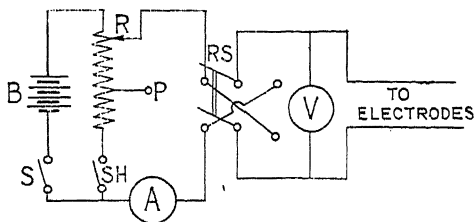


Fig. 22.—Controlled Electrode Potentials: Wiring Diagram

mercury connexion to the drive, a clamp for holding the outer electrode, and a removable and adjustable support for the beaker. The stand originally employed (*Trans. Chem. Soc.*, 1907, 91, 377) was improvised from laboratory materials. A modified form, which has been used in the writer's laboratory for many years, is shown in section in fig. 23, and a view of a commercial form of the whole apparatus in fig. 24. As explained by fig. 23, two half-inch rods  $d$ ,  $d$  of stainless steel are fitted at both ends into the stand, and serve as supports for the wooden crossbars  $p_1$ ,  $p_2$  and  $p_3$ . Of these  $p_1$  and  $p_2$  are screwed firmly to the rods, whereas  $p_3$  slides readily on them. This is attained by letting into the top and the bottom of the wood the halves of liners taken from a commercial bearing, the upper and the lower half being in each case held together by a wire suitably soldered to them. The disposition of the bearing is shown in elevation in the main drawing and

in plan at B. The bearings and rods are lubricated with vaseline. The ring *f* for supporting the beaker is fastened to the sliding bar, and its weight is suitably counterpoised by lead *c*. The bar is controlled by the leather cord *l*, which passes over the pulley *r*. The ring *b* engages in the dresser hook *a*, which is cut off short or turned up at its end, so

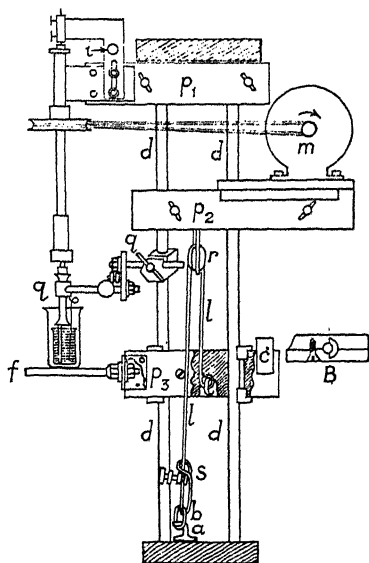


Fig. 23.—Stand for work with Controlled Electrode Potentials

that *b* may be removed from it without raising the beaker. The length of the cord *l* is made adjustable by the slip-knot arrangement shown at *s*, the loop of the slip knot being held in position as shown by a screw clip or other stop fastened to the cord. In the earlier apparatus the place of the sliding support was taken by a laboratory tripod stand.

The fitting for making connexion to the inner revolving electrode is shown in detail in fig. 25. This apparatus was originally constructed of glass tube and held in a laboratory

clamp, but is now made of metal. A steel tube  $t_1$  of about  $\frac{3}{8}$  in. external diameter is suspended by means of a washer  $w$  inside a brass tube  $t_2$ , which acts as a bearing to it. The steel tube holds the pulley  $p$  and the oil trap  $l$  and finds a continuation in the rubber pressure tube  $r$  of about  $\frac{9}{16}$  in.

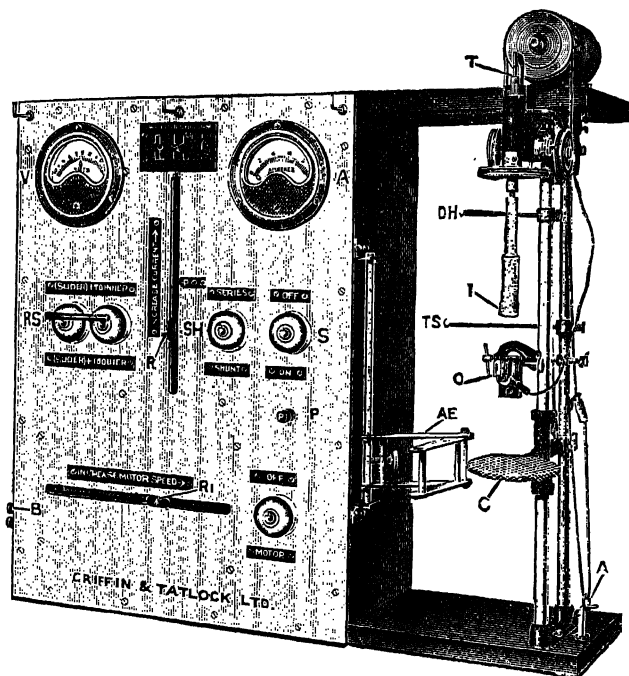


Fig. 24.—Commercial Form of the Stand

external and  $\frac{1}{8}$  in. internal diameter. A steel plug, which in the older apparatus was attached to an ordinary chuck, closes the rubber tube. Electrical connexion is made by mercury, which is poured into the hollow shaft  $t_1$  to within about 2 in. from the top, a few drops of oil being floated on this. Into the mercury dips a steel knitting needle or similar rod, which is attached to a plate holding a double terminal, shown in

fig. 23 at *i*. An ordinary chuck is apt to be rather heavy when made to grip a stem of about 4 mm. diameter. It has been replaced by a clutch, which allows instantaneous disconnexion, a matter of some importance. To construct this, the bottom of the rubber tube is slit axially (i.e. vertically) by means of a razor to a distance of about 4 cm., the slit being cut in the position shown in fig. 25 at B, so as to leave an arc of the hole of no more than 1 mm. height on one side. In

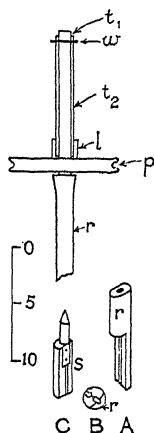


Fig. 25.—Fitting for connecting Inner Electrode.

the figures the silver is indicated by *s*, the rubber by *r*. The rubber tube can be cut in the desired fashion fairly easily if it has previously been pushed over a glass rod. Of the two thongs left hanging the thicker is cut away, thus giving the bottom of the tube the appearance shown in fig. 25 at A. The piece cut away is replaced by a semicircular segment from a  $\frac{1}{2}$ -in. silver rod. Prior to being cut, the silver rod is drilled axially for a length of about  $\frac{1}{2}$  in., the hole having the diameter of the steel plug referred to above, so that a seating is formed for this, and the silver jaw or segment may be screwed to it. The steel plug is filed flat where it is let into the silver, as shown in fig. 25 at C. It will be seen that the silver segment carries a groove of about 1 mm. depth. The steel plug is pushed home into the rubber tube so that the rubber and silver segments face each other, the latter projecting very slightly below the former. Over both is pushed a piece of close-fitting rubber tubing to a length of about 2 in., a piece of about  $\frac{3}{4}$  in. projecting. This is turned back on itself, in order to produce pressure on the segments. The rubber tubes may be wired to the steel plug by thin wire. It will be understood that an electrode or stirrer may be introduced into or removed from the clutch by simply pushing it in or pulling it out. A view of the clutch is given in figs. 23 and 24. The outer electrode is held by the clamp, which may be seen

in figs. 23 and 24, and is shown in detail in fig. 26. Electrical connexion is made through the fixed V-shaped jaw, which is advantageously lined with silver, cork being left on the movable jaw. The clamp is shown fitted with a double terminal, and insulated by ebonite in such a manner that when another similar one is placed inverted immediately above it, contact is made only by the ebonite lining, but not by metal.

The motor *m* of fig. 23 is bolted to a shelf. For a belt an elastic wire spiral is very satisfactory. The driving edge of the motor pulley should be level with the clutch pulley.

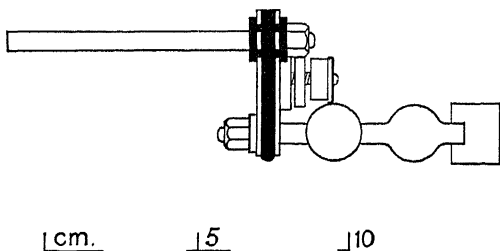


Fig. 26.—Clamp for Outer Electrode

On a 200-volt circuit the motor is satisfactorily controlled by a switch and regulating resistance of about 600 ohms, and 0.7 amp. carrying capacity. The resistance is shunted across the mains, the motor being connected to one end and the slider. In the stand shown in fig. 24 the motor is placed on the top of the stand and a pair of idle pulleys is interposed in the drive. Movable hooks *DH* and *TS* (fig. 24) are provided for suspending a thermometer and also the electrodes during drying.

#### *Adaptation of the Stand to other Electrodes.*

The foregoing stand, which was designed primarily for use with the writer's electrodes, has been described somewhat fully. It will be understood that numerous stands arranged for rotating an electrode by means of a non-flexible shaft

have been constructed for use with other electrodes. The present stand may, however, be readily adapted to most electrodes. Thus, a dish cathode may be placed on a strip of thin copper foil on the beaker support, the foil being directly connected to the spare terminal on the electrode clamp. The inner electrode clutch may frequently be used with advantage for revolving glass stirrers, if these are provided with a guide tube for the stem, which is held by the clamp. Thus the Fischer electrodes (p. 27) can be used on the stand, if an additional ordinary clamp is provided, which is placed centrally. The pair of electrodes is held by its glass tube, and connexion to the outer electrode is made by means of the usual cathode clamp, which has been adjusted at a suitable side position. Connexion to the inner electrode is made by a piece of wire from the anode terminal *i* of fig. 23.

*Several Pairs of Electrodes actuated by a Common Shaft.*

It is sometimes desired to actuate several electrodes from a single shaft. This may be accomplished in a satisfactory manner by means of the gear known as the edge wheel and disc. As the device acts also as a clutch, it can be employed to throw an electrode in or out of action while the driving shaft is kept running. The nature of the gear allows the transmission ratio to be altered readily. The writer has found a gear of this kind satisfactory during many years.

**The Auxiliary Electrode, and its Use in the  
Control of Cathode Potentials**

The importance of controlling the electrode potential by means of an auxiliary electrode in a well-stirred electrolyte, if electrolytic processes are to take place consecutively, has been discussed in Vol. I on p. 112, and the principle of placing the liquid connexion to the auxiliary electrode outside the outer electrode on p. 20. Fig. 27 illustrates a suitable electrode vessel in its stand (Lindsey and Sand, *Analyst*, 1934, 59, 329). It will be seen that the vessel proper is sealed to a

glass stem of about 15 to 18 cm. length, into the bottom of which the connecting terminal is cemented, the latter in its turn being connected to a copper wire hard soldered to the platinum lead passing through the bottom of the vessel. In use the glass stem is dropped through two holes in the two-

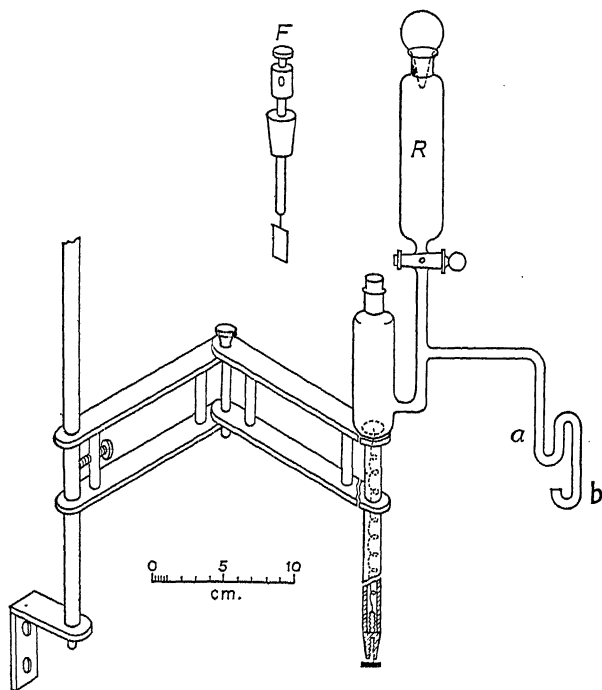


Fig. 27.—Auxiliary Electrode Vessel and Stand

armed bracket, also shown in fig. 27. Thus the electrode is held securely, but is at the same time readily adjustable for placing its tip in any position in the electrolysis beaker. Other features of the vessel are the reservoir tap funnel R, which is placed on the top of a side tube of about 6 mm. diameter, sealed about half-way up the body of the electrode



vessel. To this is attached an arm of 4 mm. bore, which has bends *a* and *b* of the shape shown. The purpose of these bends is to prevent the test solution from mixing with that in the auxiliary electrode more than avoidable, the double bend *a* being kept mainly outside the test solution, whereas the single bend *b* is inside it. The electrode vessel is closed by a tightly fitting rubber stopper, whereas a loose stopper may be placed in the reservoir funnel to prevent the access of dust. It will be seen that the electrode vessel is designed to offer a minimum of resistance in its connecting arm, a bore of 4 mm. being about the maximum which a tube may have if it is to be filled readily from above.

### *Measurement of the Cathode Potential.*

In his earlier work the writer employed the Tafel potentiometer circuit, which has been described on p. 9, for the measurement of the P.D. between the auxiliary electrode and the cathode. Lassieur in his work dating from 1923 introduced the use of a high-resistance voltmeter, represented by a galvanometer with a series resistance of 26,000 ohms (*Electroanalyse Rapide*, Paris, 1927). Lassieur recognized that his measurements were not correct, but being repeatable, they were sufficiently accurate for his purposes.

Two possible sources of error are inherent in Lassieur's technique, viz. that due to the resistance of the auxiliary electrode and that due to its polarization. As regards the former, if the resistance of the auxiliary electrode is *a*, that of the voltmeter consisting of galvanometer plus series resistance *g*, the reading of the voltmeter *v*, and the correct voltage *e*, then:

$$\frac{e}{v} = \frac{a + g}{g} \quad \text{or} \quad e = v \left( 1 + \frac{a}{g} \right). \quad (1)$$

The relative error, or the relative correction to be applied, is thus *a/g*, which quantity should be determined and kept as small as possible when the method is used. The voltmeter resistance should thus be large.

The writer uses Cambridge voltmeters of the unipivot type described on p. 2, which have a range of 0 to 1.2 volt and a resistance of 50,000 ohms. Similar instruments with a resistance of 120,000 or even of 200,000 ohms have now become available. The voltmeter is shown in fig. 28. It is fitted with an additional terminal giving access to the galvanometer alone without series resistance and may also be fitted with a spring short-circuiting key (not shown) by means of which the latter can be cut out. To prevent accidents,

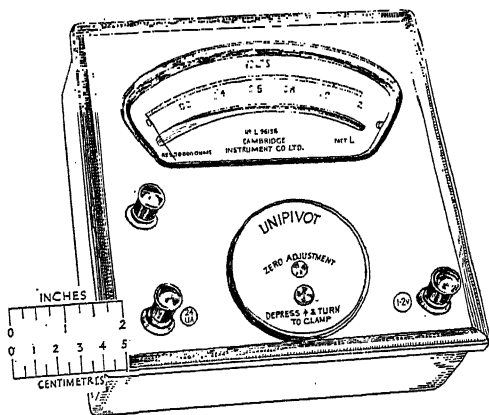


Fig. 28.—Voltmeter

such a short-circuiting key should not be fitted with a lock, and great care must be exercised not to leave it depressed when potential differences greater than about a centivolt may be present. A separate short-circuiting tapping key may equally well be connected outside the instrument.

When a voltmeter of 50,000 ohms is used with a saturated KCl electrode of the pattern described, an error of about  $-1.7$  per cent is usually made owing to the resistance of the KCl solution. If the voltmeter resistance is 120,000 ohms, the error will be only  $-0.7$  per cent. Such an error may usually be neglected in separations by graduated potential.

## ELECTROCHEMISTRY

The error discussed is avoided, and the possibility thus provided of determining  $e$  and therefore  $a/g$  of equation (1) by the use of a potentiometer in which the voltmeter plays successively the parts of the detector and the measuring instrument in the Tafel circuit (p. 9, fig. 6). The potentiometer assembly designed by the writer (*Analyst*, 1934, 59,

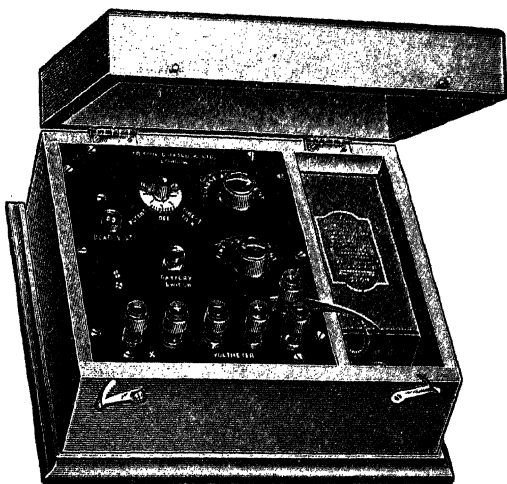


Fig. 29.—Potentiometer Assembly

328) for this purpose is illustrated in fig. 29. It is constructed largely of radio fittings, is fitted permanently with a dry cell, which is automatically cut out when the box is closed, and has been found very useful not only for the immediate purpose for which it was designed, but also for many other physico-chemical laboratory exercises. The wiring diagram is shown in fig. 30. The box is fitted with three pairs of terminals. Of these one is left permanently connected to the dry cell, the pair marked "voltmeter" is connected as indicated, and that marked  $+$  and  $-$  to the points under



trated on releasing this before depressing the Morse key M. The voltmeter then registers the P.D. between the two sliders, and hence that between the points to be measured.

It will be remembered that in the Tafel circuit the voltmeter remains in parallel with the variable points  $Sc$  and  $Sf$ , while the P.D. between the points  $+$  and  $-$  is being balanced against that between  $Sc$  and  $Sf$  with the aid of a separate zero instrument. With the present arrangement the voltmeter cannot remain shunted across  $Sc$  and  $Sf$  while it is being used as a detector instrument, and it therefore becomes necessary to examine what is the maximum error that may be introduced thereby.

If  $E$  be the total E.M.F. of the potentiometer circuit,  $X$  the P.D. between  $Sc$  and  $Sf$ ,  $R$  the total resistance, and  $r$  the resistance between  $Sc$  and  $Sf$ , then obviously  $X = Er/R$ .

When the voltmeter is placed in parallel with  $r$ ,  $X$  is altered, since both  $r$  and  $R$  undergo a slight diminution, which is manifestly the smaller the higher the resistance of the voltmeter. As the calculation of the error is somewhat lengthy, it may suffice to give only the result. It is found with sufficient accuracy that the maximum error occurs when  $r/R = 2/3$ , and is then equal to  $(4/27)ER/g$  or  $0.15ER/g$ ,  $g$  being the resistance of the voltmeter. For the dry cell we may take  $E = 1.5$  volts, for our potentiometer  $R = 250$  ohms, and for our voltmeter  $g = 50,000$  ohms. We thus find that the maximum error occurs at readings of about 1 volt and then amounts to 1.1 millivolts. Errors of this order fall within the range of accuracy of the instrument, and would be further diminished if a voltmeter of higher resistance were employed.

The potentiometer can usually replace the Cambridge portable ionization potentiometer described in Vol. III in the section on  $p_H$  measurement. As in it, the accuracy is limited by that of the voltmeter, and for readings of about 1 volt the accuracy of the two instruments should be the same. For smaller readings the absolute volt-accuracy of the Cambridge instrument increases, whereas that of the present instrument is uniform throughout.

*The Brown Auxiliary Electrode.*

The Brown auxiliary electrode (D. J. Brown, *J. Am. C. S.*, 1926, 48, 582) differs in principle from the electrodes hitherto described. It consists of the same metal as that which is being deposited, and is placed in the electrolyte outside the lines of flow of the current. If the metal were being deposited "reversibly" on the cathode no P.D. would exist between it and the Brown electrode. Neglecting metal over-voltage, the P.D. between the two electrodes at ordinary temperature is  $1/n0.0581 \log C_c/C_b$ , where  $n$  is the valency of the metal,  $C_c$  its concentration in the cathode layer, and  $C_b$  its concentration in the layer adjoining the Brown electrode. Thus, if in a bismuth solution at ordinary temperature the concentration of the metal ions in the cathode layer is one hundredth of that in the body of the solution a P.D. of about 2 centivolts will be read, and inversely, if this P.D. is consistently maintained, the concentration in the cathode layer can never be less than one hundredth of that in the body of the solution. It may also be assumed that complete exhaustion of a metal in the body of the electrolyte never takes place, and therefore, that control of the potential of a Brown electrode will automatically prevent the potential of the cathode from assuming values much more negative than such at which the metal may be said to have been removed from an analyst's point of view. Thus the Brown electrode can serve for separating metals by the method of graded potential, as has been confirmed for copper from tin, bismuth from lead and tin, antimony from tin, and tin from cadmium by Brown and by Kny-Jones (*Analyst*, 1930, 55).

From the practical point of view the method offers considerable advantage. The metal to be determined may be employed in the form of a wire, or it may be deposited at the beginning of a determination on a platinum wire, the wire in either case being weighed along with the cathode. When deposition on platinum is employed, the wire is connected through the high-resistance voltmeter to the cathode, a short-circuiting switch being placed in parallel. The latter is kept

closed for about a minute until a sufficient deposit has formed on the wire. When the switch is opened, control of the cathode potential may begin. Fig. 31 shows a silver-lined clamp for holding the wire. This is fitted through an ebonite upright to a rod or tube, allowing the whole to be supported by

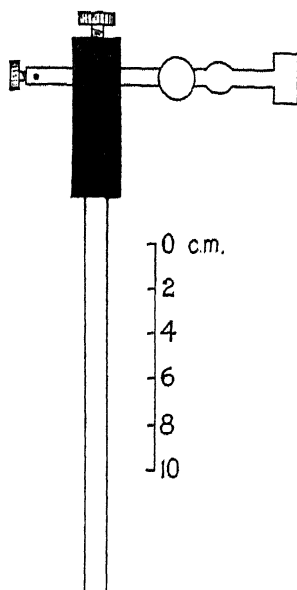


Fig. 31.—Clamp for Wire

the auxiliary electrode holder of the stand in the same way as the calomel electrode vessels. Owing to the fact that the P.D.s to be controlled do not exceed a few centivolts, a detecting instrument such as the electron-beam sectrometer described on p. 6 might probably replace the high-resistance voltmeter.

## CHAPTER II

# TECHNIQUE OF ELECTRO-ANALYTICAL DEPOSITIONS

### Assembling and Adjusting the writer's Apparatus

Mercury is poured through a capillary funnel into the tube  $t_1$  (fig. 25, p. 32) until it reaches about two inches from the top, with the contact needle in position. This is followed by a few drops of machine oil. Connexions to the battery terminals and to the mains for the motor are now made.

When the all-platinum electrodes (fig. 14, p. 21) are used, these are assembled as described on p. 21, and connexion to the flexible drive is made by pushing the stem home between the silver contact piece and the rubber holder. The guide tube and outer electrode will now remain suspended and the clamp  $q$  of fig. 23, p. 30, is set in position, so as to grip the collar and guide tube, and at the same time allow the inner electrode to revolve freely, while it is enveloped on all sides except the bottom by the outer electrode.

The height of the supporting ring  $f$  (fig. 23, p. 30) is next adjusted. It is first lowered, a beaker is pushed up from below so that its bottom almost touches the outer electrode, and the ring is then raised to support it. The leather cord is now fastened to the hook on the base, and the length of the cord adjusted by means of the special stop so as to be taut, while the support is in its proper position.

To adjust the stand for the new pattern pair of electrodes (fig. 15, p. 22), the inner electrode is inserted into its glass tripod and suspended from the clutch of the flexible drive, as in the case of the all-platinum electrodes. The outer electrode (fig. 15*b*) is introduced from below, until its lower



rim is flush with the bottom of the tripod legs. The clamp (fig. 23, p. 30) is then adjusted to grip, and at the same time make contact through the silver jaw with the tab T of the outer electrode (fig. 15). The height of the clamp should be such that the vertical distance between the lower edges of the two electrodes is about half that of the distances between their upper edges.

The adjustment of the support is the same as previously described, the outer electrode almost touching the bottom of the beaker. In disconnecting, the outer electrode is removed separately from the assembly of inner electrode and tripod, which latter may remain suspended.

The electrodes having been placed in position, the motor is adjusted to a speed of 250 to 300 revolutions per minute. Beakers in use are covered with cover plates. These may be split clock glasses, but it is easier to cut them from bakelite sheet. In the latter case the previously slotted plates are slipped over the top of the beaker so that one partially covers the other. They may be held together by a few drops of water. When an auxiliary electrode and a thermometer are employed, these should be arranged in a straight line with the stems of the electrodes, and the slots must be cut to take them also.

### The Auxiliary Electrode

The auxiliary electrode which we now recommend is the saturated KCl calomel electrode. In the literature, potential differences referred to other electrodes are often quoted. To transpose these at 18° C. to the saturated calomel electrode, proceed as follows. When referred to the N/1 hydrogen electrode, subtract 0.251 volt; when referred to the N/1 calomel electrode, add 0.035 volt; when referred to the N/10 calomel electrode, add 0.087 volt; when referred to the  $\text{Hg}_2\text{SO}_4$ , N/1  $\text{H}_2\text{SO}_4$  electrode, add 0.41 volt; when referred to a normal quinhydrone electrode add 0.453 volt (*vide* Vol. I, pp. 72 and 95). In many cases, particularly in gravimetric electrolytic analysis, the P.D.s referred to are

negative, and the positive values of the P.D. between auxiliary and working electrode are more conveniently stated than the equal and opposite ones between working and auxiliary electrode. In this case subtraction must be exchanged for addition and vice versa in the transpositions just indicated.

### *Charging the Electrode.*

The bottom of the vessel is covered by a layer of mercury. On this is poured a paste made by triturating in a mortar mercurous chloride and mercury with a saturated solution of potassium chloride. A depth of about 3 mm. should be sufficient. The electrode vessel is now filled with potassium chloride crystals nearly to the shoulder, saturated potassium chloride solution is poured in till it almost reaches the upper level of the connecting arm, and the rubber stopper is firmly inserted. Instead of the mixture of mercury and calomel made in a mortar, a very fine similar mixture prepared electrolytically according to a method described by Lipscomb and Hulett (*J. Amer. Chem. Soc.*, 1916, 38, 21) is preferably employed. Such a mixture can now be obtained commercially. The auxiliary electrode will show a sufficiently accurate potential, if all chemicals employed are the purest obtainable commercially.

The liquid in the connecting arm may be saturated potassium chloride solution, but other electrolytes can be employed when it is desired to exclude chlorides from the test solution. The connecting liquid is stored in the reservoir vessel, from which it is run into the connecting arm. The saturated potassium chloride calomel electrode is superior to other mercury standard electrodes, inasmuch as small amounts of connecting liquid diffusing into it have little influence on its potential, provided that the solution remains saturated with potassium chloride. Thus small amounts of sulphate and nitrate ion have only a negligible effect. This was confirmed by A. J. Lindsey (*Analyst*, 1934, 59, 326) by filling the body of the electrode vessel with solutions containing sulphate and nitrate ion, which at the same time were kept saturated with potassium and mercurous chloride by the presence of these

substances in the solid state. The result was that a solution of 20 gm. Glauber's salt in 100 ml. (1.2 N) showed no effect; 50 gm. sodium nitrate in 100 ml. solution (about 6 N) made the potential of the standard electrode 9 millivolts more negative.

Other points of fundamental importance in auxiliary electrodes to which the Lassieur technique is applied, are, that they should maintain a fairly constant resistance, and that they should be non-polarizable by the small currents taken by the high-resistance voltmeter. The former requirement is not satisfied, for example, by quinhydrone reference electrodes, which develop high transfer resistances in use. Mercury electrodes, on the other hand, remain constant in resistance, so long as no recrystallization of the potassium chloride crystals to a solid cake is allowed to take place. Furthermore, a saturated potassium chloride electrode has been shown to be practically non-polarizable, even when currents giving a reading of 1 volt on the 50,000 ohm voltmeter passed through it in either direction for two hours. A reference electrode recommended by Lassieur, in which the mercurous chloride, mercury paste is omitted, was shown to be unsatisfactory as regards polarizability.

#### *Measurement of the Resistance of the Auxiliary Electrode.*

The resistance of the auxiliary electrode may be readily measured by means of the high-resistance voltmeter (fig. 28, p. 37), and potentiometer box (fig. 29, p. 38), which have been described. An amalgamated zinc rod is fitted into the electrode clamp *q* of fig. 23, p. 30, and allowed to dip into a zinc sulphate solution held by a beaker standing on the beaker support. Into this dips also the tip of the auxiliary electrode. The voltmeter having been connected to the potentiometer box, the zinc rod is connected to the terminal X—, the auxiliary electrode to the terminal X+ in the box. The uncorrected reading *v* of the voltmeter is first read, the double-pole throw-over switch A (fig. 30, p. 39) having been put into the position marked "direct". The battery switch having been put on, the throw-over double-pole switch is

next put into the position marked "potentiometer", and the correct voltage  $e$  is determined as described on p. 39. The quantities  $v$ ,  $e$  and the voltmeter resistance  $g$  (usually 50,000 ohms) being known, the relative correction  $a/g$  and the resistance  $a$  of the auxiliary electrode may now be determined by means of equation (1), p. 36.

### *Performance of a Simple Deposition.*

For simple depositions, the shunt switch SH (fig. 22, p. 29) may be left open. The stirrer is started, and the solution heated to its proper temperature. The main switch is now closed, the current increased to its proper value, and allowed to flow for the prescribed time. Where possible, the complete removal of the test ion should be confirmed chemically towards the end of a deposition. When this is not possible, the time required is frequently known from previous experiments. A method often recommended is to keep part of the electrode bare during the deposition, after this is believed to be complete, to add water, and to confirm that no further deposit has been formed on the fresh part of the electrode covered. This method is specially useful for dish cathodes. Its general application is, however, limited by the fact that it is usually preferable to cover the electrode completely. Where other methods are not applicable, complete exhaustion must be tested for by electrolysis to constant weight.

When disconnecting electrodes on the writer's stand, the beaker is gripped by its rim in the left hand, and the support  $f$  (fig. 23, p. 30) is allowed to slide to its lowest position. A 5-in. evaporating basin is placed upon the support, and the beaker is then gradually lowered from the electrodes, the outer electrode being washed with a jet of water from a wash bottle or preferably from an aspirator bottle placed on the top of the stand, until it is outside the electrolyte. Only now should the motor be stopped. The washing may be continued with the electrode outside the electrolyte. The beaker is then removed, any drippings being caught by the dish, and the outer electrode is disconnected as already described. The simplest method of drying consists in dipping the electrode

successively into a jar containing alcohol and one containing ether, or successively into two jars containing acetone, the first a sample that has been used in a number of previous determinations, the second one that is fairly fresh. The alcohol may be duty-free commercial methylated, but not the ordinary methylated spirit of the shops. After the water has been replaced by volatile liquid the electrode is dried by means of a large bunsen flame waved some distance below it. During this operation the electrode is held either in the hand by a glass hook, or by a hook suitably attached to the stand. On

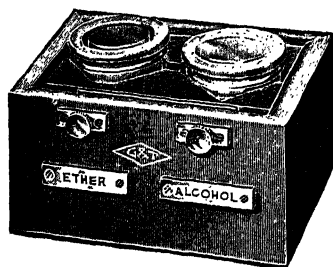


Fig. 1.—Stand for Drying Jars

no account may the current be switched off until the electrode has been disconnected. In order that the drying jars may be safe from being upset, which might lead to a fire, they should be placed in a stand such as that illustrated in fig. 1. This stand may conveniently also have accommodation for the thermometer and the cover glasses.

When electrolysis stands are employed, which do not allow the easy removal of the vessel holding the electrolyte from underneath the electrodes, the electrolyte must be gradually replaced by pure water while the current is flowing. This is done by introducing a siphon, which removes the electrolyte from the bottom, while it is being replaced by water poured in from the top. To avoid the siphon Price and Judge have suggested the use of a tap funnel as a container for the electrolyte.

### *Depositions with Controlled Potential of the Cathode.*

When the potential of the cathode is kept under control during electrolytic depositions, the auxiliary electrode is usually connected to the positive, the cathode clamp to the negative terminal of the high resistance unipivot voltmeter

(fig. 28, p. 37), the connecting wires being taken along hooks or rings at the top of the stand so as to avoid fouling other apparatus. The shunt switch is kept closed throughout the deposition, and the tip of the auxiliary electrode is placed in the beaker outside the outer electrode not less than 1 cm. below its top. After the motor has been started and the liquid taken to the proper temperature, the current is adjusted to a suitable value and the high-resistance voltmeter is read. The voltage is prevented from going above this initial value by adjustment of the slider belonging to the current rheostat. When the current has gone down to a value of usually 0.2 amp. it is increased until the voltmeter registers an increase of 0.05 volt. At this reading the voltmeter is again kept constant by adjustment of the current, until the latter has fallen to its previous lowest value. Two more increases of 0.05 volt are usually made, the last voltage being maintained for three to five minutes. For the separation by graded potential of metals that are more noble than, say, bismuth, such as silver, it would be necessary to reverse the connexions to the voltmeter, and as the metal is removed, the readings would obviously decrease instead of increasing. It may sometimes be convenient to place a reversing switch behind the voltmeter.

From what has been explained in the previous sections, it will be clear that at about 80 or 90 degrees centigrade, making the cathode more negative by about 7 centivolts, corresponds under equilibrium conditions to a reduction of the ion, if univalent, to one-tenth of its concentration. Twice this alteration of potential would cause a reduction to one-hundredth, thrice to one-thousandth, and so forth. If the metal ion is bivalent, only half the alteration of electrode potential corresponds to the same ratio of reduction in concentration; if it is trivalent, one-third of the difference of voltage will have the same effect. When a metal is being deposited under controlled potential, the ammeter usually gives a very useful indication of its removal by the current decreasing to a small residual value of about 0.2 or 0.3 amp. To make this method satisfactory, the electrolyte should

contain a reducing agent such as a hydrazine or hydroxylamine salt, as explained in Vol. I on p. 120.

Washing and disconnecting, when working with controlled potential, are carried out as already explained for simple depositions. The warnings given there, not to stop the motor before the electrodes are outside the electrolyte, and not to switch off the current before the cathode has been removed, must on no account be forgotten.

### *General Remarks.*

In electrolytic analysis the electrodes and beakers must always be kept scrupulously free from grease, and should so far as possible not be touched with the fingers. This is especially important for work with the smaller current densities, which are used when stationary electrodes are employed. If rapid results are required the bulk of the solution should be kept as small as possible.

It was formerly believed that of the simple salts only the sulphates and nitrates were applicable in electrolytic analysis. Following the work of Engels in 1896, the writer in 1908 and Schoch and collaborators in 1916, chlorides used in conjunction with hydroxylamine and hydrazine salts as depolarizers have become increasingly important. Of these two classes of compounds, hydrazine salts appear to be efficient as depolarizers under all conditions; the depolarizing efficiency of hydroxylamine is appreciably smaller, but is improved by the presence of chloride and of copper ions. In all cases, but most markedly with hydroxylamine salts at low current densities, rise of temperature increases depolarizing efficiency (Lindsey and Sand, *Analyst*, 1935, 60, 739).

In addition to their depolarizing action, hydroxylamine salts appear to have the effect of making the metal deposit more fine grained. This may possibly be connected with their property of acting also as oxidizing agents, and thus causing the production of ammonium hydroxide at the cathode. Such an action might, by locally raising the  $p_H$  of the solution, tend towards the precipitation of traces of metal hydroxide, which in their turn would act as colloids, and produce a

more fine grained deposit. The usefulness of depolarizers in electrolytic analysis appears to have been first stressed by Hollard and Bertiaux (*Analyse des Metaux par Electrolyse*, Paris, 1906).

For principles of general importance in the practice of electrolytic determinations, the reader is referred back to the sections on the practical importance of overpotential, on consecutive electrolytic processes, on residual current, and on the structure of electrolytic metal deposits contained in Vol. I.



## CHAPTER III

# QUANTITATIVE DEPOSITION AND SEPARATION OF INDIVIDUAL METALS

In the following sections we propose to give instructions for the quantitative deposition of a number of metals, and their separation from each other. As already explained, the most important basis for separations is furnished by differences of deposition potential. We propose, therefore, to arrange the metals in the order of their standard equilibrium potentials (Vol. I), taking the commoner ones first and proceeding from nobler to baser. Thus, in solutions containing only simple ions, it should be possible to separate each succeeding metal from the preceding one, if there is a difference of not less than about 0.3 volt in standard equilibrium potential. Unfortunately it is not always safe to assume that only simple ions exist in solutions even of what are commonly known as strong electrolytes. Thus cuprous ions form complexes with chloride ions, and metal and hydroxyl ions may combine in neutral solution, causing hydrolysis. Metal overvoltage also causes difficulty. It is therefore necessary to test out all separations individually. The current strength which it is safe to employ at the beginning of a deposition and the time required for complete extraction will vary with the initial concentration of the electrolyte, and with the efficiency of stirring, which in its turn depends on the type of electrodes used. We shall therefore, wheresoever possible, state type of electrode, initial amount of metal, and volume of solution in the prescriptions given, and it will be understood that divergencies, particularly regarding time, are to be looked for when other conditions are applied. The shape of the beaker is also of importance in its

effect on stirring efficiency. In general it is best to have the beaker as narrow as the electrodes and the volume of electrolyte will allow. We propose in particular to refer to the electrodes shown in fig. 14 (p. 21), as "the writer's original electrodes", those shown in fig. 15 (p. 22), as "the writer's modified electrodes", and those described on pp. 27 and 28 as "Fischer's" and "Lassieur's" electrodes respectively. Attention is again directed to the necessity of testing for complete extraction, and to the general remarks regarding technique in the preceding chapter. We are not in general stating the speed of the stirrer. This should usually be adjusted to the maximum which is considered safe with the apparatus employed. Only when residual currents cause difficulty should the speed of stirring be reduced.

### *Literature.*

Indebtedness for prescriptions is expressed particularly to the following books, from which further information may be obtained:

1. W. Böttger: *Physikalische Methoden der analytischen Chemie*, pp. 99 to 259, Leipzig, 1936.
2. A. Lassieur: *Electroanalyse Rapide*, Paris, 1927.
3. A. Fischer and A. Schleicher: *Elektroanalytische Schnellmethoden*, being vols. 4 and 5 of *Die Chemische Analyse*, Stuttgart, 1925.
4. E. F. Smith: *Electro-Analysis*, Baltimore, 1919.
5. A. Classen, tr. by W. T. Hall: *Quantitative Analysis by Electrolysis*, New York and London, 1919.
6. W. D. Treadwell: *Elektroanalytische Methoden*, Berlin, 1915.
7. A. Hollard and L. Bertiaux: *Analyse des Metaux par Electrolyse*, Paris, 1906.

For exhaustive references to the literature of Electrolytic Analysis to 1934 the reader is referred to the list compiled by B. M. Flade-Schall, which is incorporated in Böttger's monograph (No. 1 of list, pp. 235 to 259).

Equilibrium potentials are taken from the data collected

in the Reports of the deutsche Bunsen-Gesellschaft by R. Abegg, Fr. Auerbach, R. Luther and C. Drucker. As previously, concentrations are "molar", i.e. they are expressed by the symbol of the species placed in a square bracket, the unit being the weight of the symbol in grammes per litre; e.g. for  $[\text{Cu}^{++}]$  63.6 gm./litre; for  $[\text{Hg}_2^{++}]$  400 gm./litre. Specific gravities are indicated by  $d$  (density).

### Silver

Standard equilibrium potential:



#### *Deposition from Nitrate Solution.*

Silver tends to form peroxide on the anode when deposited at ordinary temperature from nitrate solution. This is avoided by effecting the deposition at boiling temperature, or by the addition of a few millilitres of alcohol at ordinary temperature. As is frequently the case with soft metals deposited from solutions of their simple salts, the crystals of silver are somewhat large and loose, and deposition on a simple platinum electrode should therefore be confined to small quantities not above 0.1 gm. The difficulty may be overcome by coating the cathode electrolytically with mercury. According to Lassieur it is best to deposit a known amount of mercury simultaneously with the silver. It is then only necessary to employ an amount of mercury of one-tenth of the weight of the silver.

*Example 1.*—Lassieur's electrodes. Solution, volume 100 ml., containing 1 to 2 ml. nitric acid of density 1.33, and a known suitable volume of a standardized solution of mercury nitrate; temperature just under boiling; current 2 amp.; time 20 min. The amalgam is washed in the ordinary way with alcohol and ether, and may be dried for a few minutes at 100°.

When the mercury is deposited electrolytically prior to silver deposition, as was done by the writer, it was found neces-

sary to employ a quantity about ten times as great as that of the silver. Moreover, owing to the volatility of the mercury, the deposit had to be dried in a current of air which was saturated with mercury vapour. This is most conveniently obtained by the use of the apparatus shown in fig. 1, in which a hand-blower, fitted with a valve at either end, is utilized to blow air in a narrow jet through some mercury. (W. J. Grant.)

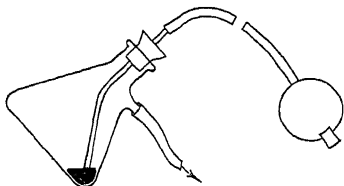


Fig. 1.—Hand-blower

*Example 2.*—Writer's original electrodes, coated with about 1.5 gm. mercury. Solution, about 0.1 gm. silver

taken as nitrate, 1 ml. concentrated nitric acid, volume 85 ml., 18 gm. tartaric acid was added as a depolarizer; temperature boiling; current started at 7 amp. decreasing during deposition to 0.2 amp., the cathode potential being controlled as described on pp. 48 and 49.

In the experiment the P.D. between the auxiliary mercury-mercurous sulphate, 2N-sulphuric acid electrode, and the cathode was regulated to 0 to 0.15 volt. When instead of this auxiliary electrode the saturated calomel electrode is employed, its potential relative to the cathode is negative throughout, and it must therefore be connected to the negative terminal of the voltmeter. The connecting liquid in the arm of the electrode must in this case contain no chloride, and may consist of a slightly acidified solution containing 50 gm. sodium nitrate per 100 ml. The potential of the cathode will decrease during deposition from about 0.4 to 0.25 volt. The time was 7 min. With the writer's modified electrodes the current is started at about 5 amp., and the time is about 10 min.

### *Deposition from Ammoniacal Solution.*

*Example 1.*—Writer's original electrodes. Solution derived from about 0.5 gm. silver, 10 ml. concentrated nitric acid, and 15 ml. concentrated ammonium hydroxide, volume 85 ml. Temperature boiling. Current started at about 3 amp., the voltage between cathode and anode, or between cathode and auxiliary electrode, being kept constant, until the current has

decreased to 0.2 amp. The voltage of cathode then made more negative by about 0.3 volt in 0.05 steps. Time under 10 min. Results very accurate.

*Example 2.*—Prescription given by Böttger. Fischer's electrodes. Solution: 3 to 5 gm. ammonium nitrate, 10 to 15 ml. concentrated ammonium hydroxide, volume 100 ml. Temperature atmospheric. Initial current 1 amp. Voltage regulation as in example 1.

### *Deposition from Cyanide Solution.*

*Example 1.*—Writer's original electrodes. Solution derived from 0.5 gm. silver, 3 ml. concentrated nitric acid, ammonium hydroxide till neutral, 2.5 gm. potassium cyanide, volume 85 ml., temperature about 90°, current started at 8 amp., voltage kept constant, current decreasing to 5 amp., time 6 min.

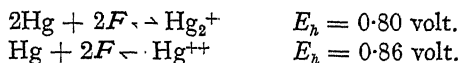
*Example 2.*—Lassieur's electrodes. Add sodium hydroxide solution, until silver hydroxide completely precipitated, re-dissolve by addition of 10 per cent potassium cyanide solution, volume 100 to 200 ml. Room temperature. Current 2 amp. Time 20 minutes.

### *Deposition from Acetate Solution.*

*Example.*—Writer's original electrodes. Solution derived from 0.5 gm. silver, 5 ml.  $\text{HNO}_3$   $d = 1.42$ , 25 gm. ammonium acetate, volume 85 ml. Temperature almost boiling. Current 3.5 to 0.2 amp., the voltage between anode and cathode being at first kept constant, and then raised in stages by altogether 0.3 volt.

## Mercury

Standard equilibrium potentials:



We have thus to consider normal potentials of both mercurous and mercuric ions. The two types are in equilibrium

with the metal, and with each other, when their equilibrium potentials are equal, i.e. for ordinary temperature, when

$$0.80 + 0.029 \log [\text{Hg}_2^{++}] = 0.86 + 0.029 \log [\text{Hg}^{++}],$$

or when the ratio  $[\text{Hg}_2^{++}]$  to  $[\text{Hg}^{++}]$  equals approximately 100. We thus see that, whether mercurous or mercuric salts are used in electrolysis, an equilibrium will establish itself in the cathode layer of a solution, from which mercury is being deposited, of such a nature that the concentration of the mercurous ions will be about a hundred times as great as that of the mercuric. A peculiarity of mercuric halogen compounds is their slight ionization. Thus, if a solution of mercuric chloride is electrolysed, a considerably more negative cathode potential is required for complete extraction than is the case for a solution of mercurous nitrate.

When electrolytically deposited, mercury shows some tendency to alloy with platinum. It is therefore advisable to coat platinum electrodes with silver from a cyanide bath before depositing mercury on them. Mercury is deposited from cold nitrate solution first in large drops, which are unsuited for weighing, but when the potential of the cathode is made negative enough for the evolution of hydrogen, the mercury spreads out as a mirror. It is interesting to note that from ammoniacal or cyanide solutions mercury is obtained in small adherent drops; a comparison between the electro-deposition of mercury and silver thus leads to the conclusion that large drops correspond to large crystals, and small drops to small crystals. In cases in which conditions are imposed that would lead to the formation of large loose drops the cathode should be coated with a mirror of mercury before a determination. When mercury mirrors are to be dried, they may be dipped into alcohol and ether, or into acetone, though this procedure may lead to loss, when applied to loose deposits (Classen-Hall, p. 135). Dry ether may be evaporated from a mercury deposit by a current of ordinary air, but it is safer to employ the device shown for silver (fig. 1, p. 55). If the cathode is kept covered with electrolyte, there is no fear of loss during electro-deposition owing to the volatility

of the mercury, except perhaps during prolonged and very vigorous evolution of hydrogen.

Mercury may be deposited from the following solutions: nitrate, chloride, ammonium hydroxide, potassium cyanide, sodium sulphide (useful for cinnabar analysis), potassium iodide (useful for mercuric iodide preparations).

#### *Deposition from Nitrate Solution.*

*Example.*—Writer's original electrodes. Solution derived from 0.6 gm. mercury,  $1\frac{1}{2}$  ml.  $\text{HNO}_3$   $d = 1.42$ , volume 85 ml. Temperature warm. Current 9 amp., volts, anode-cathode 2.6 to 3.7. Time 5 min.

#### *Deposition from Chloride Solution.*

*Example.*—Lassieur's electrodes. Solution contains 5 ml.  $\text{HCl}$   $d = 1.19$ , 1 gm. hydroxylamine hydrochloride, various amounts of mercury, volume 100 ml. Current 2 amp. Temperature slightly under boiling. Time 20 min.

#### *Deposition from Ammoniacal Solution with Controlled Potential.*

*Example.*—Writer's original electrodes. Solutions derived from about 0.5 gm. mercury, 10 ml.  $\text{HNO}_3$   $d = 1.42$ , 20 ml.  $\text{NH}_4\text{OH}$   $d = 0.88$ , volume 85 ml. Temperature slightly under boiling. Current 3, decreasing to 0.2 amp., volts saturated calomel to cathode 0 to 0.10. Time 6 min.

#### *Deposition from Potassium Iodide Solution.*

For estimation in Hydrarg. cum creta (S. G. Liversedge, *Quart. J. Pharm.*, 1929, 2, 243), dissolve sample of about 1 gm. in  $\text{HNO}_3$ , add sufficient KI to form a clear solution of the double salt. Precipitate the calcium by addition of a little sodium acetate and sufficient sodium oxalate, heat, filter through a Gooch crucible, wash, and then make strongly alkaline with NaOH. Writer's original electrodes. Volume 85 ml. Current 6 amp. Temperature  $80^\circ$ . Time 10 min.

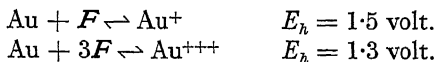
#### *Deposition from Sodium Sulphide Solution.*

*Example.*—R. O. Smith (*J. Amer. Chem. Soc.*, 1905, 27, 1270). Dish cathode, stirrer 900 revolutions per minute. Dis-

solve mercuric sulphide corresponding to 0.2 gm. mercury in 7 to 10 gm. crystallized sodium sulphide, add 5 gm. crystallized sodium sulphite. Volts: anode-cathode 2.4 to 2.5. Amp.: 3.5 decreasing to 0.3. Time 15 to 20 min.

## Gold

Standard equilibrium potentials:



From these values it follows that in the presence of metallic gold the ratio of equilibrium concentrations is given by:

$$1.5 + 0.058 \log [\text{Au}^+] = 1.3 + 0.058 \log [\text{Au}^{+++}]^{\frac{1}{3}}$$

or  $[\text{Au}^{+++}] = 2.2 \times 10^{10} [\text{Au}^+]^3$  (approximately) at ordinary temperatures.

It is thus only at very small concentrations of auric ions that aurous ions need be considered. Gold has been satisfactorily deposited for analysis from the chloride, the cyanide, and the thioaurate solution. We give only:

### *Deposition from Chloride Solution.*

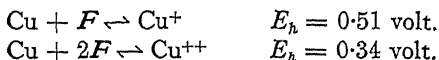
*Example.*—Lassieur's electrodes. Solution derived from 5 ml. HCl  $d = 1.19$ , 1 gm. hydroxylamine hydrochloride, volume 100 ml. Temperature ordinary. Current 2 to 3 amp. Time 20 min.

The cathode potential is very much more negative than would be required for the deposition of gold from a solution of its simple ions. No doubt the metal is present mainly in the form of complex anions. According to T. M. Perkin and W. C. Prebble (*Electrochemist and Metallurgist*, 1904, **3**, 490), to remove a deposit of gold from a platinum cathode, it is treated with a dilute solution of potassium cyanide, to which some hydrogen peroxide has been added.



## Copper

Standard equilibrium potentials:



Hence cuprous and cupric ions are in equilibrium with metallic copper at ordinary temperature, when

$$\begin{array}{l} 0.51 + 0.058 \log [\text{Cu}^+] = 0.34 + 0.058 \log [\text{Cu}^{++}]^{\frac{1}{2}}, \\ \text{or when} \quad [\text{Cu}^+] = 1/1000 [\text{Cu}^{++}]^{\frac{1}{2}} \text{ approximately.} \end{array}$$

Cuprous ion in equilibrium with cupric ion of ordinary strength at a copper cathode thus has a relatively low concentration. Nevertheless its presence may be of importance. Thus if the  $p_{\text{H}}$  of the solution is too great, the process may take place:  $2\text{Cu}^+ + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$ , leading to the deposition of cuprous oxide on the cathode, and thus to a high analytical result. Again, cuprous ions are of importance in solutions containing anions capable of combining with them to form complex cuprous ions. The most striking instance of this kind is afforded by the cyanide ion. Here the formation of complexes such as  $\text{Cu}(\text{CN})_2^-$ , &c., leads practically to the total suppression of simple copper ions, cupric ions being reduced to the intermediate cuprous stage by the oxidation of cyanogen ions to cyanogen. In solutions containing chloride ions, complex formation likewise takes place, so that considerable quantities of copper are left in solution during deposition, in the form of complex cuprous ions, after the concentration of the cupric ions has sunk to negligible proportions. Thus an appreciably more negative cathode potential is required for the complete analytical extraction of copper from a solution containing chloride ions than from one in which only sulphate and nitrate are present.

The analytical electro-deposition of copper is of considerable historical interest, this metal having been the first to be estimated quantitatively by electrodeposition in 1864 by Wolcott Gibbs, and independently by Luckow in 1865. The

ease with which it may be quantitatively deposited in an adherent form from the most diverse solutions, has made the electrolytic deposition of copper one of the most widely used methods for its estimation. As regards possible sources of error the formation of cuprous oxide has already been referred to. Similarly, cupric hydroxide may form in solutions devoid of acid. When hydrogen is evolved at the end of a deposition from a sulphate solution containing free acid, the last traces of copper are deposited in a powdery form which is somewhat loose, though sufficiently adherent to allow it to be washed without loss. The appearance of this form suggests that it has been produced by the decomposition of a hydride primarily formed. According to Lassieur approximately 10 ml. of hydrogen may be extracted per gramme of such metal by heating it in a vacuum. In agreement with this view of the role of hydrogen, the deposition of the last traces of copper in a powdery form is suppressed, when the cathode potential is kept under control, so as to prevent the liberation of hydrogen, and also by the addition of oxidizing agents such as nitric acid to the electrolyte. The last-named method is frequently employed. When copper has been brought into solution by means of nitric acid, lower oxides of nitrogen must be removed by evaporation, or by the addition of urea or of salts of hydrazine or of hydroxylamine. As is well known, nitric acid in low concentration shows little action on copper, but in the presence of oxides of nitrogen, the action is so rapid that the metal deposit cannot be washed without appreciable loss.

#### *Deposition from Sulphate and Nitrate Solutions.*

*Example 1.*—Writer's original electrodes. Solution derived from 0.25 gm. copper, 1 ml. concentrated  $\text{H}_2\text{SO}_4$ , 0.5 ml.  $\text{HNO}_3$   $d = 1.42$ , volume 85 ml. Ordinary temperature. Current 10 amp., reduced to 5 amp. when the solution becomes colourless. Time about 5 min.

*Example 2.*—Writer's modified electrodes. Amounts of copper,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$  the same as in example 1, volume about 60 ml. Ordinary temperature. Current 7 amp., reduced

to  $3\frac{1}{2}$  amp. when the solution has become colourless. Time 15 to 20 min. Instead of the platinum cathode, a silver cathode, preferably of size sufficient to surround the glass tripod, may be used. Volume of liquid about 100 ml. Time 15 to 20 min. For stripping the copper from the silver electrode, see p. 10.

*Example 3.*—As examples 1 and 2, except that the nitric acid is omitted. In its place further additions of sulphuric acid may be made. As already explained, the last traces of copper are usually deposited in a powdery condition without impairment of the result. The deposition of the pulverulent form may be avoided by keeping the cathode potential more positive than that at which hydrogen is liberated. Hydrazine or hydroxylamine sulphate may be added to reduce the residual current.

*Example 4.*—Förster's prescription. No artificial stirring. Sulphuric acid concentration about twice normal. Temperature  $70^{\circ}$  to  $80^{\circ}$ . Volts limited to 2 by the employment of a single accumulator cell.

### *Deposition from Chloride Solution.*

*Example.*—(E. P. Schoch and D. G. Brown, *J. Amer. Chem. Soc.*, 1916, **38**, 1660.) Fischer's electrodes. Solution derived from 0.4 gm. copper, 8 to 12 ml. concentrated HCl  $d = 1.20$ , 2 gm.  $\text{NH}_2\text{OHHCl}$ , volume 150 to 220 ml. Temperature of solution started at  $70^{\circ}$  and then left to itself. Cathode potential against normal calomel electrode limited to  $-0.40$  volt. Current 5 amp., decreasing almost to zero, at 2 to 1.2 volts between anode and cathode. Time 15 min. As explained above, if cupric chloride is started from, the solution becomes colourless as the copper deposits, owing to reduction of the ions to the cuprous condition, but considerable quantities of copper may still be in solution, which are subsequently gradually removed.

In addition to the solutions referred to, cyanide, oxalate, and ammoniacal solutions have been employed under suitable conditions for the quantitative deposition of copper.

### Bismuth

Normal equilibrium potential:



Although bismuth may be deposited in an adherent form electrolytically, difficulties often arise, owing to sponge formation. This is sometimes the result of the deposition of products of hydrolysis arising from a local increase of hydroxyl ion concentration, or it may be due to the production and subsequent decomposition of a hydrogen compound of the metal. In some cases the difficulty can be overcome by controlling the cathode potential. If the electrolyte is stirred efficiently enough, e.g. with the writer's original electrodes, and if the solution contains a sufficient concentration of nitric acid, the metal may be deposited quantitatively in an adherent form without control of the cathode potential by means of a current of 2 to 3 amps. Another point of importance in bismuth deposition for analysis is the necessity to employ reducing agents to prevent the formation of pentoxide on the anode. These reducing agents also serve the important purpose of keeping the residual current down, and thus making the ammeter a trustworthy indicator for the completion of the analysis. In sulphuric acid solution the tendency to the formation of basic salts makes it impossible to work at any but very high acid concentrations. However, from a hot solution containing about one-fifth of its volume of concentrated sulphuric acid and a small amount of hydrazine sulphate, a good adherent deposit may be obtained under conditions of controlled potential. When free chlorides are present, it is practically impossible to obtain coherent deposits unless special precautions are taken to inhibit the formation of basic salts. According to F. G. Kny-Jones (*Analyst*, 1939, 64, 172) the difficulty may be overcome by the addition of free oxalic acid, which acts as a solvent for the basic salts. In the absence of oxalic acid, chlorides should be excluded from the electrolyte, and it is advisable to replace the calomel

electrode by the 2N sulphuric acid mercurous sulphate mercury electrode and use a junction liquid consisting of sodium nitrate solution. Since electro-deposited bismuth tends to alloy with platinum, it is useful to protect the cathode by plating it with silver from a cyanide solution. Records exist of the quantitative deposition of bismuth from acid solutions containing nitric, hydrochloric, tartaric, citric and acetic acid, and from alkaline solutions containing tartrate plus cyanide.

### *Deposition from Nitrate Solution.*

*Example 1.*—Writer's modified electrodes. Solution derived from 0.25 gm. bismuth, 3 ml.  $\text{HNO}_3$   $d = 1.42$ , 0.1 to 0.2 gm. hydrazine sulphate, volume 50 to 60 ml. When the solution from which the bismuth is being deposited contains lead, the presence of sulphate must be avoided, and instead of the hydrazine sulphate, four or five drops of a 50-per-cent solution of hydrazine hydrate should be added to the electrolyte, followed by enough nitric acid to clear the solution if a precipitate forms. Temperature  $80^\circ$  to  $85^\circ$ . Current 1.3 to 0.2 amp. Cathode potential to twice normal sulphate electrode (see above), with junction liquid of about 10 gm.  $\text{NaNO}_3$  in 100 ml. water,  $-0.45$  to  $-0.60$  volt (p. 49). Time 25 min.

*Example 2.*—Writer's original electrodes. Employed in the analysis of "Sobita", i.e. bismuth sodium tartrate. (S. G. Liversedge, *Quart. J. Phar.*, 1929, 2, 243.) The solution is derived from 0.5 to 1 gm. bismuth sodium tartrate, 2.5 ml.  $\text{HNO}_3$   $d = 1.42$ , volume about 100 ml. Current 2 amp., which was gradually reduced so as to inhibit gas evolution. Temperature about  $70^\circ$ . Time 10 min.

### *Deposition from Chloride Solution.*

*Example.*—F. G. Kny-Jones (*loc. cit.*). Writer's modified electrodes. Solution derived from 0.25 gm. bismuth dissolved in concentrated hydrochloric acid  $d = 1.16$ , containing a small amount of nitric acid. The electrolytic test solution of volume 100 ml. contained a little more than 10 ml. concentrated HCl, also 5 gm. oxalic acid and 0.5 gm. hydrazine hydrochloride. Temperature  $80^\circ$  to  $85^\circ$  C. Current regulated so that initial potential of the cathode to the auxiliary calomel electrode was not more negative than 0.15 to 0.17 volt. Later, when the

current had almost fallen to zero, the cathode potential was brought in steps of 0.02 volt to a value of  $-0.25$  to  $-0.30$  volt. Time 15 to 20 min.

The Brown auxiliary electrode may also be used. A platinum wire of about 0.3 mm. diameter was placed in parallel with the cathode, and plated along with the latter by means of a current of 0.2 amp. for about 30 sec. as described on pp. 41 and 42. After opening the short-circuiting switch there referred to, the potential of the wire was kept at 0.02 to 0.03 volt. In a series of experiments the current started at 0.4 to 0.25 amp., the time varied from 20 to 30 min.

#### *Deposition from Sulphate Solution.*

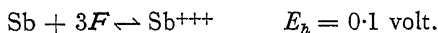
*Example.*—F. G. Kny-Jones (*loc. cit.*). Solution obtained by dissolving the metal in concentrated sulphuric acid, sometimes with the addition of one-tenth of its volume of nitric acid. The test solution, volume about 100 ml., contained 20 to 25 ml. concentrated sulphuric acid and 1 gm. hydrazine sulphate. Temperature about  $100^{\circ}$  C. Cathode potential to saturated calomel electrode  $-0.055$  volt taken in steps to  $-0.15$  volt. Amount of substance 0.13 to 0.25 gm. Current started at 0.4 to 1.2 amp., and taken to practically zero. Time 10 to 30 min.

#### *Deposition from Tartrate Solution.*

*Example.*—Writer's original electrodes. The solution was derived from about 0.4 gm. bismuth oxide, 2.5 ml.  $\text{HNO}_3$ ,  $d=1.42$ , 12 gm. sodium tartrate, volume 85 ml. Temperature almost boiling. Current 3 to 0.2 amp. Cathode potential against 2N  $\text{H}_2\text{SO}_4$  electrode  $-0.65$  to  $-0.80$  volt, i.e. against saturated calomel electrode  $-0.25$  to  $-0.40$  volt. Time 12 min.

### Antimony

Standard equilibrium potential:



The difficulties which arise in the deposition of antimony are probably due mainly to its metalloid character. Thus in sulphuric acid solutions hydrolysis prevents complete solution

except when the acid is highly concentrated, and even then it is necessary to add hydrazine sulphate to prevent oxidation from the antimonous to the antimonie state. In hydrochloric acid solutions reduction from the antimonie state takes place much more readily, and hydrolysis is not so troublesome. According to Lassieur, antimony deposited from antimonous chloride solution is loose, unless the cathode potential is controlled with great care. The loose deposits are attributed to the intermediate formation of stibine, analogous to results already discussed in regard to copper and bismuth. From a pentachloride solution, however, good deposits are easily obtained. A phenomenon peculiar to antimony deposits is their tendency to hold non-metallic elements, such as the halogens, oxygen and sulphur. These phenomena have already been discussed in Vol. I, p. 121. To avoid the inclusion of chlorine from chloride solutions, the temperature must be maintained above  $70^{\circ}$ . Ordinarily thio-salts yield inclusions of oxide and sulphide, but according to Lassieur no excess weight is found, when an amalgamated cathode is employed. The explanation given is that the smoothness of the electrode prevents the occlusion of alkali salts. Possibly, and as it seems to the writer more probably, the mercury surface may prevent the adherence of colloidal particles. Antimony in the antimonie state is not deposited from aqueous alkaline solutions nor from fluoride solutions, facts that are made use of in separating it from other metals. Antimony has been quantitatively deposited from sulphuric acid, hydrochloric acid, tartaric acid and sulphosalt solutions.

#### *Deposition from Sulphate Solution.*

*Example.*—Writer's original electrodes. Solution derived from about 0.5 gm. antimony, 40 ml. concentrated sulphuric acid, 40 ml. water, 0.5 gm. hydrazine sulphate. Temperature about  $110^{\circ}$ . Current 4 to 0.3 amp. Cathode potential to 2N  $\text{H}_2\text{SO}_4$  auxiliary electrode  $-0.50$  to  $-0.65$  volt. It is necessary to interpose a sulphuric acid solution of sufficient strength to avoid boiling in the connecting limb of the auxiliary electrode vessel. Time 20 min.

*Deposition from Chloride Solution.*

*Example.*—Lassieur's electrodes. The antimony is supposed to be originally present in the antimonous state in a solution containing about 5 ml.  $\text{HCl}$   $d = 1.19$  of volume 25 to 50 ml. This is heated on the water bath, and potassium chlorate is added, until the yellowish green colour due to chlorine is seen. The chlorine having been boiled off, another 5 ml. to 15 ml. of concentrated hydrochloric acid, and 1 gm. hydroxylamine hydrochloride are added, and the liquid is brought to a volume of 150 to 200 ml. Temperature about  $70^{\circ}$ . Current starting at 2 amp. The P.D. cathode-saturated calomel electrode is more positive than  $-0.4$  volt. Time 20 min.

*Deposition from Sulphantimonite Solution.*

*Example.*—Lassieur's electrodes, plated with about 0.1 gm. mercury from a nitrate solution. The antimony in the form of sulphide is dissolved in 80 ml. sodium sulphide solution  $d = 1.14$ . Potassium cyanide solution equivalent to 5 gm. KCN, is added, in order to prevent the formation of polysulphides, which dissolve metallic antimony; volume 100 to 130 ml. Temperature ordinary. The current is started at 1.5 amp., the P.D. anode-cathode being kept approximately constant, and the current reduced during the electrolysis accordingly. Time about 35 min.

*Deposition from Tartrate Solution for the determination of antimony in tartar emetic.*

*Example.*—(S. G. Liversedge, *Quart. J. Pharm.*, 1929, **2**, 243.) Writer's original electrodes. The solution is derived from 0.5 to 1 gm. tartar emetic dissolved in the minimum amount of water, 3 gm. tartaric acid, 2 gm. Glauber's salt and 0.5 gm. hydrazine sulphate; volume 80 ml. Temperature about  $80^{\circ}$ . Current 3 amp. Time 15 min.

*Removal of antimony from a Platinum Cathode.*

This is most readily effected by heating in a solution of dilute nitric acid containing tartaric acid.



### Arsenic

Although the application of electrolysis to the detection of arsenic was proposed by Fischer as early as 1812, yet it is only quite recently that success in its quantitative deposition as metal has been attained. The difficulty is doubtless due to the non-metallic character of the element, as a result of which it does not form simple ions in solution to a measurable extent. Further, owing to the possibility of arsine formation, the cathode potential permissible for deposition is confined within narrow limits. The determination of traces of arsenic as hydride in the electrolytic Marsh test will be discussed later in a special section.

At the suggestion of the writer, the well-known Reinsch test for arsenic was studied by S. Torrance (*Analyst*, 1938, 63, 104). Reinsch recognized in 1841 that the presence of hydrochloric acid was necessary for success. In recent times B. S. Evans (*Analyst*, 1923, 48, 357, 417) investigated the reaction underlying the test. Torrance confirmed the fact that while copper displaces arsenic from N/1 HCl solution at 50° C., no positive result is obtained under similar conditions with normal sulphuric acid. In order to obtain a positive result with the latter acid, solutions of about 20 N. strength must be employed at boiling temperature. It thus appears that the formation of complex ions is essential to the deposition of arsenic, and that such ions are formed more readily in hydrochloric than in sulphuric acid solution. The experiments also confirmed that Reinsch's test yields no positive result for compounds of quinquivalent arsenic even in hydrochloric acid solution at 50° C. On boiling, a positive result can, however, be obtained.

Torrance's experiments showed that only traces of arsenic can be deposited on a platinum cathode from arsenious chloride. On the other hand, when copper is also present in an amount about five times as great as the arsenic, the latter metal may be deposited quantitatively as copper arsenide,

the potential of the cathode being controlled, in order to prevent the formation of arsine.

When arsenic is present in the quinquevalent state, it must be reduced to the trivalent condition before it can be deposited as metal. The experiments also confirmed the fact, previously recognized by Lassieur and others, that when copper is deposited under ordinary conditions from sulphate or nitrate solutions containing arsenic, it is obtained free from the latter metal. This obviously suggests a ready method for separating copper from arsenic.

The explanation of Torrance's results may be sought in the following three assumptions: (1) Un-ionized arsenic compounds are not reduced in aqueous solution except by nascent hydrogen of high overpotential. (2) Ions containing arsenic in any form are practically absent from dilute sulphuric acid or nitric acid solutions. (3) In chloride solution anions such as  $\text{AsCl}_4^-$ ,  $\text{AsOCl}_3^{--}$ , &c., are present which are fairly readily reducible. Indications of the presence of such ions have been obtained in experiments on migration carried out in the writer's laboratory by A. C. Penney.

*Example 1.*—To the solution containing arsenic as arsenious chloride in quantity not greater than 50 mgm., were added 15 ml. hydrochloric acid  $d = 1.16$ , 1 gm. hydrazine hydrochloride, and a measured amount of a standard copper solution containing not less than 0.25 gm. copper either as sulphate or as chloride. Volume 150 ml. Temperature  $50^\circ \text{C}$ . P.D. saturated calomel electrode-cathode: 0.4 volt. Current about 4 amp. decreasing to 0.1 amp. Time about 20 min. The combined weight of the copper plus arsenic is determined, and the weight of the latter found by subtracting that of the former.

When the amount of arsenic is greater than 0.05 gm., a second measured amount of copper solution containing not less than 0.25 gm. copper is added after the electrolyte has become colourless, and the electrolysis is continued as just described.

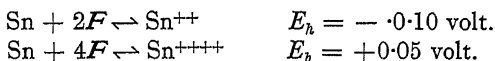
*Example 2.*—As example 1, but the original solution contains copper as well as arsenic. In this case, original copper plus copper added plus arsenic are determined as in example 1,

but an independent determination of the copper is necessary. For this purpose the weighed deposit is dissolved in a mixture of 5 ml. sulphuric acid  $d = 1.82$ , 5 ml. nitric acid  $d = 1.42$ , and 10 ml. water; the oxides of nitrogen are boiled off, 1 gm. hydrazine sulphate is added, the solution diluted to 150 ml., and the copper determined at  $50^\circ \text{C}$ . at an auxiliary potential of 0.40 volt. Time 20 min. The weight of original deposit minus weight of copper found equals weight of arsenic. The weight of copper found minus weight of copper added equals weight of copper originally present.

*Example 3.*—The arsenic is present either wholly or partly in the quinquevalent state. In this case the solution is made acid with sulphuric acid, and reduced by boiling for 5 or 10 min. with 5 ml. of a saturated sulphurous acid solution. The further procedure is the same as that detailed in examples 1 and 2.

## Tin

Standard equilibrium potentials:



Hence stannous and stannic ions are in equilibrium with the metal at ordinary temperature, when

$$-0.10 + \frac{1}{2} \times 0.058 \log [\text{Sn}^{++}] = 0.05 + \frac{1}{4} \times 0.058 \log [\text{Sn}^{++++}]$$

or, when

$$[\text{Sn}^{++++}] = 4.5 \times 10^{-11} [\text{Sn}^{++}]^2 \text{ approximately.}$$

The equilibrium concentration of stannic ions in the presence of metallic tin is thus always negligible. We conclude that, when solutions of stannic compounds are in equilibrium with metallic tin, the latter is present in solution not in the form of stannic ions, since these would be reduced to the stannous condition, but as complex ions, or as other complexes. It has been known since the time of Berzelius (1817) that stannic compounds occur in at least two forms, the  $\alpha$  and the  $\beta$ . Of these, the latter are more difficult to reduce. They

are produced from the former in feebly acid and alkaline solution on prolonged standing. In dealing with stannic solutions it must therefore not be forgotten that their properties may have been affected adversely from the electro-analyst's point of view by having been allowed to stand for prolonged periods. Hydrochloric acid appears to aid in the breaking up of complexes, and it has therefore been found useful to add this reagent along with hydroxylamine hydrochloride in certain cases at the end of a deposition, in order to secure the precipitation of the last traces of metal. Certain metals, e.g. antimony, copper and antimony copper alloys greatly promote by catalytic action the reduction of stannic to stannous tin in hydrochloric acid solution. Tin, like other metals, is deposited in a more fine-grained form, the more complex its compounds, and the more electro-negative therefore the deposition potentials are; thus deposits from stannous chloride solution tend to be somewhat loose, whereas those from stannic oxalate solution, particularly if prepared from solutions containing stannic acid, are fine-grained. Tin has been determined by electro-deposition from the following solutions among others; stannous and stannic chloride, acid and alkaline oxalate, sulphostannate.

Before depositing tin on platinum electrodes they should be coated with copper. For the removal of tin deposits a hot mixture of hydrochloric and oxalic acids may be employed. When reduced from hydrochloride solution, amounts of tin below about 0.01 gm. should be deposited on a cathode previously coated with tin or lead, so that the necessary overvoltage may be ensured.

According to A. C. Penney (private communication) freshly deposited tin shows a great tendency to dissolve in acid solution during washing. This may be inhibited by neutralizing the solution with ammonia before disconnecting. In experiments on the micro scale Penney uses 50 per cent hydrazine hydrate solution. Penney's instructions for macro-scale work are given in example 2 of depositions from hydrochloric acid solutions.

*Deposition from Hydrochloric Acid Solution.*

*Example 1.*—(Schoch and Brown, *J. Amer. Chem. Soc.*, 1916, **38**, 1660.) Fischer's electrodes. The solution is derived from quantities of tin up to 0.7 gm., dissolved in contact with metallic platinum in 10 ml. HCl  $d = 1.20$  and 4 gm. hydroxylamine hydrochloride. Volume 200 ml. Temperature  $30^{\circ}$  to  $70^{\circ}$  C., which latter temperature must not be exceeded. Current 1.5 amp. Time about  $1\frac{1}{2}$  hr. The deposit is improved by electrolysing first at constant auxiliary potential, and allowing the latter to rise after most of the metal has been deposited. According to Anna Engelenburg (*Z. anal. Chem.*, 1923, **62**, 257) 2 gm. hydroxylamine hydrochloride is sufficient at  $30^{\circ}$ , whereas at  $70^{\circ}$  a quantity as great as 6 gm. should be employed.

*Example 2* (above, modified by A. C. Penney).—Writer's modified electrodes, cathode copper plated. Samples of tin varying from 0.2 to 0.3 gm. were dissolved in 10 ml. HCl  $d = 1.16$  in the presence of about 1 gm.  $\text{NH}_4\text{Cl}$  at ordinary temperature. The solution was oxidized with a few drops of saturated potassium chlorate, the temperature being kept well below  $70^{\circ}$  on account of the volatility of stannic chloride; 4 gm. of hydrazine hydrochloride or sulphate were added and the volume was made up to 150 ml. Temperature  $35^{\circ}$  C. Current 1.5 amp. Time 30 min. Before disconnecting, the electrolyte was made just alkaline to phenolphthalein by the addition of 0.88 ammonium hydroxide.

*Deposition from Acid Oxalate Solution.*

*Example 1.*—(Sveda and Uzel, *Coll. Czech. Chem. Comm.*, 1929, **1**, 203.) Fischer electrodes, cathode copper plated. To solutions of stannous tin containing quantities of the element up to 0.5 gm., 10 gm. ammonium oxalate, 5 gm. oxalic acid crystals, and 2 gm. hydroxylamine hydrochloride are added; volume 150 ml. Temperature  $60^{\circ}$  to  $70^{\circ}$ . Current 5 amp. at 2.5 to 3.5 volts. Time 25 min.

*Example 2.*—Writer's original electrodes. Solution was made from a stock solution obtained by dissolving tin in concentrated sulphuric acid, neutralizing with ammonium hydroxide, so that the solution contained about 5 gm.  $(\text{NH}_4)_2\text{SO}_4$ , then acidified with  $\text{H}_2\text{SO}_4$ , and about 3 gm. oxalic acid added. Volume 80 ml. Temperature  $70^{\circ}$  to  $80^{\circ}$ . Current 3 to 5 amp.

Time 20 to 40 min., according to age of solution. Deposit taken to<sup>s</sup> constant weight. Cathode potential to 2N H<sub>2</sub>SO<sub>4</sub> electrode -0.9 to -1.3 volt.

### *Deposition from Sulphostannate Solution.*

*Example.*—(W. D. Treadwell, modified by Sveda and Uzel, *loc. cit.*) Revolving gauze cathode. The solution contains 0.1 gm. tin, which must be in the stannic form, either as stannic sulphide, or as stannic ammonium chloride. To this are added 6 gm. Na<sub>2</sub>S, 5 gm. NaOH, 10 ml. saturated bisulphite solution—to prevent the formation of polysulphides—and 10 gm. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>—to reduce the  $p_H$  of the solution. Volume 150 ml. Temperature 60°. Current 1.7 to 0.7 amp. at about 1.8 volt. Time about 45 min. Results usually slightly high.

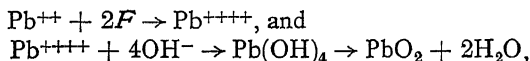
## Lead

Standard equilibrium potential:



Lead may be determined as metal or as peroxide. In the former case reducing agents must be added, to prevent the formation of peroxide on the anode, and conversely in the latter oxidizing substances such as nitric acid in sufficient concentration, or copper ions, must be present, to prevent the deposition of metallic lead on the cathode. Metal deposits from nitrate solutions tend to form loose crystals, but coherent layers are obtained from the more complex solutions. Platinum cathodes should be plated with silver or copper before depositing lead on them. Lead coatings must be washed and dried very quickly on account of the oxidizability of the metal.

The electrolytic determination of lead as peroxide is preferable to that as metal. The anode process in the formation of peroxide is probably represented by the system of ionic equations:



or, by the more general statement, that plumbous is oxidized to plumbic salt, and the latter undergoes hydrolysis. In conformity with the equations given, lead peroxide is always thrown down in a more or less hydrated condition, the water being held tenaciously. The older method of preparing the deposit for weighing was to heat it to a temperature above  $200^{\circ}$ , but even so, it was not anhydrous, and an empirically determined correction factor had to be applied. According to the writer's experiments, equally good results are obtained by depositing with a high current density at a temperature near boiling. Under such conditions electric endosmosis expels most of the water from the deposit, and it may be dried by dipping into the alcohol and ether jars in the ordinary way. A suggestion to convert the lead peroxide into the monoxide by ignition before weighing is, according to experiments by A. J. Lindsey, not practicable owing to the fact that at the temperature required, lead monoxide is appreciably volatile. Reducing agents, including nitrous acid, which may have been formed during the solution of the metal, must be carefully excluded. It must also not be forgotten to have the electrode entirely free from grease, in order that the deposits may adhere well.

#### *Deposition as Peroxide from a Nitrate Solution.*

*Example.*—Writer's modified electrodes. Outer electrode anode. The solution, if obtained from metallic lead, must be freed from oxides of nitrogen by boiling. It contains 10 ml.  $\text{HNO}_3$   $d = 1.42$  in a volume of 85 ml. Temperature  $90^{\circ}$  to  $95^{\circ}$ . Current 5 amp. Time about 10 min. for about 0.3 gm. lead. Electrodes dried in the ordinary way. Conversion factor for  $\text{PbO}_2$  to Pb 0.863, instead of the theoretical value 0.866.

To remove a lead peroxide deposit from a platinum anode after electrolysis, it may be warmed with dilute nitric acid, to which a little of a suitable reducing agent, such as hydrogen peroxide, sodium nitrite, oxalic acid, metallic copper, &c., has been added.

*Deposition as Metallic Lead from an Alkaline Tartrate Solution.*

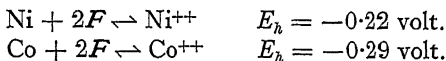
*Example.*—Writer's original electrodes. The solution is derived from 1 ml. concentrated nitric acid, 20 gm. tartaric acid, and is made alkaline with 20 ml. concentrated ammonium hydroxide. Volume about 120 ml. Temperature almost boiling. Current 2 to 3 amp. Time about 10 min. for 0.3 gm. lead.

*Deposition as Metallic Lead from a Chloride Solution.*

*Example.*—Lassieur's electrodes. The solution contains 20 ml. concentrated hydrochloric acid, and 2 gm. hydroxylamine hydrochloride in 125 ml. Temperature 70°. To complete the electrolysis, the beaker is cooled to ordinary temperature by placing it in a trough of cold water. Time about half an hour for about 0.2 gm. lead. For determining very small quantities the cathode should be plated with lead before electrolysis, so that the requisite overpotential may be obtained.

**Nickel and Cobalt**

Standard equilibrium potentials:



As is well known, nickel and cobalt are chemically very similar, so that the closeness of their standard equilibrium potentials is not surprising. The principal chemical difference between them is the greater tendency of cobalt derivatives to pass into the trivalent state. Salts of trivalent cobalt are readily hydrolysed in feebly acid solution with the precipitation of  $\text{Co}_2\text{O}_3$ . This tendency forms the basis of a proposal put forward by A. Coehn and M. Gläser (*Z. anorg. Chem.*, 1903, 33, 9) for the anodic separation of cobalt and nickel. Attempts to elaborate a practicable method based on this proposal, however, failed owing to the difficulty of preventing cobalt from depositing on the cathode. This difficulty was overcome by S. Torrance by employing the writer's diaphragm inner electrode. Details of the application of this method are given on pp. 25–26 and 97–98.



Nickel or cobalt may be quantitatively extracted from solutions of their simple salts, to which buffer mixtures of acetic or of formic acid and their sodium salts have been added. The use of these buffer mixtures is, however, accompanied by a tendency of the metal to be deposited in a carbonaceous form, and therefore for high results to be found. Very accurate results, on the other hand, are obtained in the electrolytic determination of nickel from strongly ammoniacal solutions, containing ammonium conductivity salts. Such solutions may be derived from the sulphate, chloride, or nitrate of the metal. In cobalt deposition from ammoniacal solution, there appears to be a tendency to the formation of rough deposits, which is probably connected with the oxidation of the cobaltous-ammine ion. This tendency can be counteracted by the use of reducing agents, such as sodium formate, or by controlling the cathode potential. Another electrolyte, which has been employed in electrolytic nickel and cobalt determination particularly in separations from chromium, aluminium and manganese, is the ammonium oxalate solution. Sometimes difficulty is experienced in stripping nickel from a platinum cathode. In this case anodic solution of the metal in warm dilute nitric acid is best applied.

#### *Deposition from Ammoniacal Solution.*

*Example 1.*—(S. G. Liversedge, *Quart. J. Pharm.*, 1930, 3, 482.) Writer's original electrodes. The solution is derived from about 0.125 gm. metallic nickel, dissolved in boiling moderately strong HCl; 5 gm.  $(\text{NH}_4)_2\text{SO}_4$ , 25 ml. concentrated  $\text{NH}_4\text{OH}$  solution are added. Volume 70 ml. Temperature ordinary. Current 4 amp. Time 15 min.

*Example 2.*—Writer's modified electrodes. About 0.2 gm. nickel as sulphate, 1.5 gm.  $(\text{NH}_4)_2\text{SO}_4$ , 25 ml. concentrated  $\text{NH}_4\text{OH}$  solution were present in a volume of 125 ml. Temperature about  $75^\circ$ . Current 5 amp. at 10 volts. Time 20 min. Exhaustion tested for by dimethylglyoxime test.

*Example 3.*—Dish cathode. About 0.3 gm. cobalt as sulphate, 20 ml. concentrated  $\text{NH}_4\text{OH}$  solution, and 3.5 ml. 94 per cent acid were present in a volume of 125 ml. Temperature warm. Current 6.5 amp. at 7 volts. Time 20 to 30 min.

*Deposition from Ammonium Oxalate Solution.*

*Example.*—Dish with revolving disc anode. The solution is derived from about 0.3 gm. nickel as sulphate, and 15 gm. ammonium oxalate. Volume 125 ml. Temperature about 95°. Current 8 amp. at 5 volts. Time 50 min.

**Cadmium**

Standard equilibrium potential:



From the relatively negative value of its equilibrium potential we conclude that the deposition of cadmium is dependent on its hydrogen overpotential. On platinum cathodes this overpotential cannot be relied upon to establish itself, when the amount of the metal is very small, and in such cases the cathode must be coated with cadmium before use by plating from a cyanide bath. It is usually recommended to protect platinum from alloy formation with deposited cadmium by coating it first with silver or copper. Probably an amalgamated copper gauze cathode, analogous to the Paweck amalgamated brass electrode, should be suitable for cadmium deposition. Cadmium has been deposited for purposes of electrolytic analysis from acid, neutral, and alkaline solutions. When nitrates are present, free strong acids must be absent. In cyanide or other alkaline solutions, small amounts of nitrate may be present.

*Deposition from Sulphuric Acid Solution.*

*Example.*—(Davison, *J. Amer. Chem. Soc.*, 1916.) Dish and spiral anode stirrer. The solution is derived from amounts of  $\text{CdSO}_4$  up to 0.6 gm. and 0.5 ml. concentrated  $\text{H}_2\text{SO}_4$ . Volume about 100 ml. Temperature started boiling, then left. Current 3 to 4 amp. at about 12 volts. Time about 10 min.

*Deposition from Hydrochloric Acid Solution.*

*Example.*—(Schoch and Brown, *loc. cit.*) Fischer electrodes. Quantities of cadmium, up to 0.3 gm. taken as chloride, were dissolved in 200 ml.  $H_2O$ , 2 gm. hydroxylamine hydrochloride were added and the solution was slightly acidified with HCl. Temperature ordinary. Current 1 amp. Time 40 to 60 min.

*Deposition from Acetate Solution.*

*Example.*—Writer's original electrodes. The solution was derived from about 0.15 gm. cadmium as sulphate and 2 ml. concentrated  $H_2SO_4$ . It was then made alkaline, the metal precipitated as hydroxide by means of NaOH ( $3\frac{1}{2}$  gm.), and then acidified and cleared with glacial acetic acid (about  $1\frac{1}{2}$  ml.). The  $p_H$  of the solution should be adjusted by the addition of sodium acetate, or if necessary acetic acid, to the value at which methyl orange has just turned from yellow to red. Volume 80 ml. Temperature about  $80^\circ$ . Current 4 to 1 amp. at a P.D. between cathode and auxiliary 2N.  $H_2SO_4$  electrode of  $-1.12$  to  $-1.20$  volt.

*Deposition from Cyanide Solution.*

*Example.*—Dish and spiral anode stirrer. The solution was derived from about 0.5 gm. cadmium as sulphate, 5 gm. NaOH, and 2 gm. KCN (sufficient to clear the solution). Volume about 120 ml. Temperature hot. Current 5 amp. Time about 15 min.

**Iron**

Standard equilibrium potential:



Although the standard equilibrium potential of iron differs little from that of cadmium, it may be expected that owing to its small hydrogen and large metal overpotential, hydrogen will be liberated in preference to the metal from acid solution. In agreement with this, it has hitherto not been found possible to deposit iron quantitatively from solutions of its simple salts on a platinum cathode. Success may, however, be attained

by the use of a mercury cathode. The residual current produced by the alternate oxidation and reduction of the ions of this metal at the two electrodes is also a source of difficulty. The most satisfactory electrolyte is the ammonium iron oxalate solution elaborated by Classen, although the deposited iron often contains carbon. According to Classen, this is due only to reduction of the ammonium carbonate formed by oxidation of the ammonium oxalate at the anode, and may be avoided by not continuing the electrolysis unnecessarily long. The electrolytic determination of iron is found useful in separating it from metals such as aluminium, chromium, &c. The iron may be present either in the ferrous or in the ferric state. In the former case the double oxalate is yellowish red, in the latter case it is light green in colour. Nitrate must be expelled from the solutions. In all cases exhaustion of the electrolyte must be tested for by oxidizing a sample with a drop of nitric acid and adding a considerable excess of hydrochloric acid and sulphocyanide.

*Deposition of Iron from Ammonium Oxalate Solution.*

*Example 1.*—Iron present in the ferrous condition. (A. Fischer.) Dish with revolving plate anode, 600 rev./min. About 0.2 gm. ferrous ammonium sulphate was dissolved in a small amount of water, and the solution poured into a stirred solution of 7.5 gm. ammonium oxalate in water. Volume 120 ml. After electrolysis has proceeded for 15 min., oxalic acid in the form of 0.2 ml. of a saturated solution is added in 3 min. intervals to replace the acid oxidized at the anode. Temperature about 85°. Current 7 amp. at about 6 volts. Time 30 min.

*Example 2.*—Iron present in the ferric condition. (F. Exner, *J. Amer. Chem. Soc.*, 1903.) Dish with revolving spiral anode, 800 rev./min. The solution is derived from 0.25 to 0.5 gm. iron ammonium alum, and 7.5 gm. ammonium oxalate. Volume 125 ml. Temperature hot. Current 7 amp. at 7.5 volts. Time 25 to 35 min.

*Deposition into a Mercury Cathode from a Sulphate Solution.*

*Example.*—(E. F. Smith.) Howard's apparatus (p. 14). Revs. of anode 500 to 900 per minute. The solution contained

about 0.2 gm. iron as ferrous sulphate, and 3 drops concentrated  $\text{H}_2\text{SO}_4$  (40 drops = 1 ml.) in about 40 ml. Temperature ordinary. Current 3 to 4 amp. at about 7 volts. Time 7 min.

### Zinc

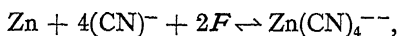
Standard equilibrium potential:



Zinc has the most negative equilibrium potential of any metal that is electro-deposited on solid cathodes in gravimetric analysis. It can be deposited quantitatively from solutions containing free strong acids only into mercury cathodes. The remarks made with regard to cadmium about the difficulty of removing traces of metal from acid solutions by means of platinum cathodes hold in increased measure for zinc. Such electrodes should therefore be coated with zinc by deposition from a cyanide bath, when tests for traces have to be made. As with cadmium it is usually recommended to coat platinum with either copper or silver before use, in order to prevent alloy formation. The best electrode to employ for zinc deposition appears to be the Paweck amalgam electrode. It may be used in the writer's modified design of cathode, the diameter being chosen so as to allow it to be slipped over the glass tripod, in order to obtain as uniform a current density as possible (see p. 25). A convenient way to amalgamate this brass electrode is to dip it into a 5 per cent mercuric chloride solution containing a little free nitric acid. It is then heated in dilute hydrochloric acid, which brightens the grey deposit of mercury. Alternatively the electrode may be amalgamated by electro-depositing mercury from a slightly acidified nitrate solution with high current density (see p. 57). Drying after washing with alcohol and ether should be carried out in a current of air saturated with mercury vapour by means of the device shown in fig. 1, p. 55. According to Böttger ammonium salts must be excluded from solutions intended for use with the Paweck electrode, since with these, owing to intermediate formation of am-

monium amalgam disintegration of the mercury surface takes place. By the use of the Paweck electrode, the occlusion of zinc oxide in the last layers of the deposit is prevented. This is no doubt due to the fact that with this electrode discharge of zinc ions takes place preferentially to that of hydrogen ions during the whole deposition. Thus there is no possibility of the solution turning alkaline in the electrode layer, while zinc ions are still present therein. To remove the zinc after deposition hydrochloric acid is employed.

Oxidizing substances must be absent from solutions to be used for depositing zinc. Thus nitric acid must be removed from all acid baths. Small amounts of nitrate in alkaline solution are, however, not harmful. Thus, according to Lassieur, nitric acid in quantities up to 1 ml. acid of density 1.33 per 125 ml. solution may be present without harmful effect in the cyanide bath specified below. On the other hand, potassium cyanide must not be present in too great concentration in this bath, or the electrode potential necessary for the complete deposition of the zinc becomes unattainable. This may be understood from a consideration of the equilibrium potential of zinc in cyanide solution, similar considerations applying to the complex cyanide ions of other metals. We have the electrode equation:



from which, and equations (4a) and (5) (Vol. I, p. 80):

$$\begin{aligned} E &= E_0 + \frac{1}{2} \times 0.058 \log \frac{[\text{Zn}(\text{CN})_4^{--}]}{[(\text{CN})^-]^4} \\ &= E_0 + 0.029 \log [\text{Zn}(\text{CN})_4^{--}] - 0.116 \log [(\text{CN})^-] \text{ volt.} \end{aligned}$$

We thus see that a tenfold increase of cyanide ion concentration makes the equilibrium potential more negative by about 0.12 volt. It is probable that the complete extraction of the zinc is dependent on the cyanide ion concentration in the electrode layer being kept below a certain low value by migration from the cathode under the influence of the current, and that this cannot be attained when the original

cyanide concentration is too high. According to Lassieur's experiments the maximum amount of potassium cyanide permissible in 125 ml. solution is about 1.5 gm.

When acetate baths are employed, the  $p_H$  of the solution should be about 4.5, i.e. as high as possible conforming to the condition that no basic salt is produced in the cathode layer. During electrolysis, however, the average  $p_H$  of the solution tends to change in opposite directions for several reasons. At the cathode, liberation of zinc in preference to hydrogen tends to lower the  $p_H$ , liberation of hydrogen to raise it; at the anode, liberation of oxygen lowers the  $p_H$ , replacement by oxidation of acetate by carbonate ion tends to raise it. It is thus comprehensible that working under certain conditions the writer found a tendency for acetate solutions from which zinc was being deposited to become alkaline, whereas Lassieur, using slightly different conditions, found that his solutions became acid. In both cases the  $p_H$  of the solution was restored towards the end of a deposition, the writer adding acid, until drops of the solution, placed on litmus paper, showed a slightly acid reaction, while Lassieur added alkali, until bromophenol blue, which was placed in the electrolyte, showed a violet tinge.

Zinc has been electro-deposited for analysis from acid sulphate, formate, acetate and citrate solutions and also from ammoniacal, sodium hydroxide and cyanide solutions. The sodium zincate solution, prepared by dissolving zinc hydroxide in sodium hydroxide, is claimed by some writers to give very good results, while others working under slightly different conditions have not been successful. The reason for this divergence is probably to be sought in the presence in the zincate solution of colloidal zinc hydroxide, which would make the results dependent on very carefully controlled conditions, and in particular would militate against the use of high current densities.

#### *Deposition of Zinc from Acetate Solution.*

*Example 1.*—Writer's modified pattern of Paweck cathode, see above. To the solution of  $ZnSO_4$ , derived from about

0.20 gm. zinc, acid corresponding to 1 ml. concentrated  $\text{H}_2\text{SO}_4$  is added. This is neutralized with NaOH, and enough excess added to redissolve the precipitated  $\text{Zn}(\text{OH})_2$ . Four drops of 50 per cent hydrazine hydrate are added. The  $\text{Zn}(\text{OH})_2$  is then first reprecipitated completely and then just redissolved by the addition of acetic acid. Volume 80 ml. The beaker is placed in a small glass trough containing water and ice which is accommodated on the ring of the stand. Temperature of electrolyte about  $15^\circ$ . Current 2 amp. Time about 30 to 40 min. Throughout the deposition the solution is kept just acid to litmus paper. The zinc may be removed from the cathode by heating with dilute hydrochloric acid.

*Example 2.*—Lassieur's electrodes, or the writer's modified pattern with Paweck cylinder slipped over the tripod, see above. Add 5 ml. glacial acetic acid to the acid or neutral solution containing the zinc, then some drops of bromophenol blue, and NaOH solution, until the indicator shows a violet colour. Volume of the solution 200 ml. Room temperature. Current about 3 amp. After 20 min. some more bromophenol blue is added, and sufficient NaOH solution to restore the violet colour. Time 30 to 40 min.

#### *Deposition of Zinc from Cyanide Solution.*

*Example.*—Lassieur's electrodes, copper plated. To the solution containing about 0.4 gm. zinc,  $\text{NH}_4\text{OH}$  or NaOH solution is added to incipient precipitation, then 1 gm. KCN, and 20 ml. of 20 per cent  $\text{NH}_4\text{OH}$  solution. Volume 125 ml. Room temperature. Current 3 amp. Time about 30 min.

### Other Elements

Electrolytic methods of estimation have been studied for a considerable number of elements, which, so far as the writer is aware, have received little application. We shall confine ourselves to a summary.

#### *Cations.*

The following elements have been determined as metals, in most cases by rapid as well as by slow methods: platinum,



palladium, rhodium, tellurium and indium. Selenium has been precipitated jointly with copper. Chromium has been estimated as amalgam, and it is possible that the same method might be extended to other metals that cannot be satisfactorily deposited as such. A number of metals, having so negative a deposition potential that hydrogen is liberated in their stead at the cathode, can nevertheless be estimated as hydroxides, when deposited from solutions of sufficiently high  $p_H$ . In this case the metal ion combines with hydroxyl ion from the solution, and the hydrogen ion with which the latter was associated is discharged at the cathode. Cases in point are the deposition on the cathode of molybdenum and vanadium as hydroxides. Uranium in a similar way may be deposited as uranyl hydroxide, the uranyl radicle in this case taking the part of the element both as ion and in the hydroxide.

Like lead, a number of metals may be determined by deposition in the form of higher oxides on the anode. As with lead, the ion of the element may be considered to have its valency increased by charges from the anode, after which it combines with hydroxyl ions to form hydrated oxide. Cases in point are the estimation of manganese and thallium as higher oxides. In both cases difficulties are met with in obtaining the oxide in a sufficiently adherent form, and the  $p_H$  of the solution must be kept above a certain minimum value.

The determination of the alkali metals, and their separation from the alkaline earth metals by means of the Hildebrand apparatus, have been discussed on pp. 11 and 14.

### *Anions.*

The idea of determining anions by depositing them as insoluble salts originated with Vortmann (Monatshefte, 1894), who deposited halogens on a silver anode. Later Specketer, using Vortmann's anodes, separated iodides, bromides and chlorides from each other by the method of controlled potential (*Z. anorg. Chem.*, 1899, **21**, 273). Instead of solid silver anodes, platinum gauze electrodes, which have been plated with silver, may be employed with advantage, as was done

by Hildebrand (see p. 13). The latter considerably extended methods of estimation for anions forming insoluble silver salts. Thus carbonates, ferro- and ferricyanides, and phosphates were determined by him. The use of cadmium plated anodes for the determination of sulphides may also be recalled here.

The electrolytic destruction of nitric acid by reducing it to ammonium salts in acid solution on a copper cathode has been utilized by Vortmann (*Ber.*, 1890, **23**, 2798) for the elaboration of an electrolytic method for determining nitrates. (For fuller details of the estimations summarized in this section the reader is referred particularly to the books of Classen-Hall and Edgar F. Smith. See list of literature on p. 53.)

## CHAPTER IV

### SEPARATIONS

The principles underlying electrolytic separations which depend on the various methods of controlling the cathode potential, and on a proper selection of the composition of the solution, have already been discussed, Vol. I, pp. 111-115, and Vol. II, p. 49. In some cases the deposition of a metal as peroxide on the anode is also usefully employed. It will therefore now only be necessary for us to discuss the metals in the sequence of their ionic deposition potentials, pointing out, as far as possible, difficulties which arise, and also possibilities that are afforded by the formation of complex salts and by other circumstances.

#### **Separation of Silver and Mercury from Copper, Bismuth, Lead, Cadmium, Zinc, and other Metals.**

##### *Silver or Mercury.*

Silver and mercury are appreciably more noble than all other metals excepting gold and the platinum metals. Either of the first mentioned metals can therefore be separated from the others by the method of controlled cathode potential, provided that solutions of nitrates can be used. This can be done with all metals except tin and antimony, and these may be kept in solution by means of tartaric acid. Conditions for the separation of silver are given in *Example 2*, p. 55. The conditions of *Example 1*, p. 54, are no doubt also suitable, if the cathode potential is controlled as stated in *Example 2*. The same conditions may be employed for the separation of

mercury, and for the separation of mercury plus silver from the other metals.

The difference between the normal deposition potentials of silver and copper being very considerable (about 0.45 volt), it is possible to separate these metals merely by controlling the P.D. between anode and cathode. Thus silver may be separated from copper in the acetate solution specified on p. 56 either by keeping the P.D. cathode-saturated calomel electrode more positive than 0.3 volt or by regulating the P.D. anode-cathode not to exceed 1.25 volt. It will be understood that where special chemical reasons do not interfere, the conditions for the separation of silver from copper in simple ion solution may *a fortiori* be applied to its separation from metals more base than copper.

In the case of mercury we have also to consider its deposition from chloride solution (p. 58). This may be useful, when it has to be separated from metals such as antimony and tin. According to Lassieur the P.D. for its complete extraction from a solution containing antimony must be made about 0.1 volt more negative than in the absence of this metal. It is, however, probable that the antimony has no effect on the deposition potential of mercury, but that the instruction given by Lassieur is based on the fact that mercury requires a more negative deposition potential from a chloride solution than from one in which it is more completely ionized.

Silver has also been separated from copper in ammoniacal solution (see *Example 1*, p. 55), the P.D. saturated calomel electrode-cathode being kept below 0.10 volt. In this case the presence of cupric salt is the cause of a large residual current, so that the complete removal of the silver from solution must be tested for chemically. The use of the diaphragm anode would no doubt improve matters. According to Lassieur the conditions given on p. 56, *Example 2*, for the deposition of silver from cyanide solution also ensure its separation from copper. It will be understood that silver may also be separated from platinum in cyanide solution. For the necessity of controlling the amount of cyanide in the solution, see the discussion under zinc, p. 81.

*Separation of Silver from Mercury.*

Owing to the closeness of silver to mercury in the electro-potential series, there appears to be little prospect of success for a purely electrochemical method of separation. A chemical method is therefore indicated. Thus about 0.4 gm. of a mixture of about equal parts of the metals was deposited and weighed. The deposit was dissolved in a boiling solution containing 20 ml. nitric acid,  $d = 1.4$ , and the liquid made faintly alkaline with sodium hydroxide, and then faintly acid with nitric acid. Potassium cyanide was then added until the liquid was clear. After warming slightly, the silver was precipitated with nitric acid, allowed to settle, and collected. The silver cyanide was then dissolved in a solution containing 3.5 gm. potassium cyanide per 100 ml., and the silver precipitated at about  $80^\circ$  with a current of 3 amp.

It is probable that the difference in behaviour of silver and mercury to iodide will furnish the basis of a good method of separation.

**Separation of Copper, Bismuth and Antimony from Subsequent Metals.**

The standard equilibrium potentials of copper, bismuth, and antimony are too close to allow these metals to be separated from each other in solutions of their simple salts. We have already seen that they may be separated from the nobler metals, silver and mercury, in solutions containing mainly simple ions. We now have to consider their separation from the baser ions of lead and tin. Such separations will involve those from all baser metals.

*Bismuth and Copper from Lead.*

Bismuth may be separated from lead in nitrate solution according to the conditions laid down in *Example 1*, p. 64, and the same conditions may be applied to the separation of copper from lead.

*Antimony from Lead.*

The standard equilibrium potential of antimony ion being about 0.1 volt less positive than that of bismuth ion, there is some difficulty in separating it from lead in simple ion solution. Nevertheless, according to Lassieur a separation may be effected from chloride solution under the conditions specified on p. 67, if the concentration of the lead does not exceed 2 gm. per litre. The upper value given there for the hydrochloric acid concentration should be employed. It is, however, probably preferable to employ one of the methods given below, converting the antimony into a complex antimonide compound and depositing the lead alone either as metal or as peroxide.

*Copper and Antimony from Tin.*

Antimony may likewise be separated from tin in chloride solution by the method described on p. 67. In this separation the current is employed not only for the deposition of the antimony, but also for the reduction of stannic to stannous ions. This reduction is catalysed by metallic antimony, and hence, after the cathode has become covered with this metal at an auxiliary saturated calomel electrode potential of 0.40 volt, a considerable increase in current takes place. The reduction must be allowed to proceed until a residual current of about 0.3 amp. has been in operation for about 5 to 15 minutes according to the size of the beaker employed.

The separation of copper from chloride solution may be carried out practically in the same way as that of antimony. The instructions given on p. 62 may be followed, or the separation may be carried out in the cold.

Good separations of antimony from tin may also be achieved in sulphate solution under the conditions specified on p. 66. Another method of separation is that from sulphantimonite solution as described on p. 67.

*Bismuth from Tin and Lead.*

Bismuth may be separated from tin and lead from chloride solutions according to the method of Kny-Jones given on pp. 63 and 64. Either the saturated calomel or the Brown auxiliary electrode may be employed. Quantities of up to approximately 0.3 gm. bismuth have been separated from about the same amount of tin plus lead.

**Separation of Copper, Bismuth and Antimony from each other.***Copper from Bismuth.*

We have already stated that the three metals copper, bismuth and antimony cannot be separated from each other electrolytically in solutions of their simple salts. Separations may, however, be effected by employing suitable complex compounds. Thus by the use of tartrate solutions containing conductance salts and free tartaric acid the deposition potentials of copper and bismuth may be separated sufficiently to allow the former metal to be removed from traces of the latter at boiling temperature. A better separation is, however, obtained by means of the combined use of tartrate and cyanide in alkaline solution. In such an electrolyte both metals are soluble, but the sequence of their deposition potential is reversed, bismuth being deposited first. In the writer's original experiments formaldehyde was added to the electrolyte to prevent deposition of bismuth pentoxide on the anode. According to F. G. Kny-Jones (*Analyst*, 1939, 64, 172) this is unsatisfactory, since precipitation of  $\text{Cu}_2\text{O}$  is usually produced. The formaldehyde has been satisfactorily replaced by hydroxylamine sulphate.

*Example.*—Writer's modified electrodes, saturated calomel electrode with sodium nitrate connexion. The solution contained originally about 0.2 gm. of bismuth and 0.25 to 0.5 gm. of copper in the form of nitrate. About 3 gm. KOH were added, the precipitated hydroxides were dissolved by 2 gm. sodium tartrate, and 2 to 3 gm. potassium cyanide were added to de-

colorize the solution completely. The volume was made up to 100 ml., and 1 gm. hydroxylamine sulphate was added. Temperature about 75° C. The P.D. saturated calomel electrode-cathode started at 0.75 to 0.77 volt, and was taken finally to 0.85 volt. The current was started in different experiments at from 0.4 to 1 amp., and fell in each case to almost nil. Time according to initial current, 10 to 25 min.

### Separation of Metals from Antimony by Conversion of the latter into Complex Antimonic Ions.

Antimony may be separated from many metals if use is made of the fact that it cannot be deposited from aqueous alkaline antimonate solutions containing tartrate. We give as an instance its separation from traces of lead.

*Example.*—Test of a sample of tartar emetic for lead. To 5 gm. sample dissolved in water, 3 gm.  $\text{KHCO}_3$  were added, and the antimony was then oxidized completely with a solution of iodine in KI. Then 4 gm. KOH, and 2 to 3 gm. tartaric acid were added. After diluting, the lead was deposited in the cold on a copper-coated cathode.

Another complex anion which furnishes the possibility of separating other metals from antimony is the antimonic fluoride ion. In order to prevent any reduction of the latter ion, it appears to be necessary to have some chromic acid or similar oxidizing agent such as vanadic acid present. The following conditions are prescribed by Lassieur for determining the copper in a deposit of copper antimony alloy, obtained by electrolysing a chloride solution containing the two metals.

*Example.*—The deposit is treated with a mixture of 5 ml. concentrated HF and 5 ml.  $\text{HNO}_3$   $d = 1.33$ , in which it dissolves instantaneously. The liquid is diluted to 100 ml., and concentrated bichromate solution is added till a yellow coloration becomes apparent. The copper is deposited at ordinary temperature. Current 1 amp. The weight of antimony is calculated by difference. The slight attack of the hydrogen fluoride on the glass beaker need cause no apprehension. It is, however, preferable to avoid pyrex glass beakers, when working with hydrogen fluoride.



Bismuth is separated from antimony in the same way as is copper, but in this case the potential of the cathode should be controlled, in order to prevent the formation of a spongy deposit.

Lead may be separated from antimony as peroxide, the two metals being first deposited together and then dissolved, after which the antimony is converted into the complex fluoride.

*Example.*—Lassieur's electrodes. The two metals are deposited together under the conditions given on p. 75 for lead, the combined deposit is then dissolved in a mixture of 30 ml.  $\text{HNO}_3$ ,  $d = 1.33$ , and 5 ml. concentrated  $\text{HF}$ . After diluting to 100 or 125 ml., bichromate solution is added, till a yellow coloration is visible, and the lead peroxide is deposited within 20 min. by a current of 2 amp. This method is applicable only in the absence of tin.

In conclusion it should be mentioned that copper may be separated completely from antimony if the latter is in the antimonic condition in a solution containing only free tartaric acid, under the conditions given for the separation of copper from traces of bismuth at boiling temperature.

### Separation of Lead from other Metals as Peroxide.

The method for determining lead as peroxide given on p. 74 is applicable to its separation from metals such as copper, cadmium and zinc, that do not tend to form deposits of higher oxides on the anode. It may also be applied to the separation of lead from silver, since silver peroxide is unstable at boiling temperature. It is, however, only suitable for the separation of lead from metals such as bismuth, antimony and tin, after these have been converted into stable complexes such as the fluoride complex.

### Notes on Arsenic.

When arsenic is present in solutions containing no chloride, it does not deposit with copper under controlled potential, as explained on p. 68. When chlorides are present the arsenic should be removed with copper, as likewise explained. It is doubtful whether arsenic in the quinquevalent condition is

ever deposited with other metals from acid solution in the absence of chlorides, and it may be taken as certain that it is never deposited from alkaline solutions of arsenates.

### **Separation of Lead and Tin from Cadmium and the Baser Metals.**

We have already discussed the separation of the nobler metals from lead and tin, and we now come to the separation of the latter metals from the baser ones, nickel, cobalt, cadmium, and therefore also iron and zinc.

Although nickel and cobalt have a less negative standard equilibrium potential than cadmium, yet according to Lassieur they behave in acid solution as baser metals, possibly as a result of the formation of complex anions. A separation of lead and tin from cadmium will therefore include that from the other metals. According to Lassieur either tin or lead may be separated from cadmium according to the conditions specified for the separation of lead from chloride solution on p. 75, if the cathode potential is not allowed to become more negative to a normal calomel electrode than  $-0.480$  volt.

As Lassieur's auxiliary electrode potentials are not corrected for the resistance of the connecting arm, this value will probably require correction.

#### *Separation of Lead from Tin.*

For the separation of lead from tin, use is made of the fact that, like quinquivalent antimony, quadrivalent tin is capable of forming very stable complexes with fluorine. Lassieur describes two procedures for utilizing this. In the first, hydrogen fluoride is added to the solution of the chlorides of the two metals, and the lead is deposited as metal, the potential of the cathode being less negative than a suitably chosen value. From the residual liquid the tin is deposited after breaking up the fluoride complex. This is achieved by causing the fluorine to combine with boric acid to fluoboric acid, and at the same time converting the tin into the stannic ammonium oxalate compound according to *Example 2*, p. 72.

A preferable method consists in depositing the tin and

lead together according to the prescription given on p. 75 for the deposition of lead from a chloride solution, weighing the combined metals, and then dissolving them in a mixture of nitric and hydrofluoric acid. The lead is now deposited alone as lead peroxide.

*Example.*—After depositing the metals together, and weighing, as just stated, the cathode is treated with a solution containing 5 ml.  $\text{HNO}_3$ ,  $d = 1.33$  and 5 ml. 40 per cent HF and 15 ml.  $\text{H}_2\text{O}$ , which dissolves the deposit instantaneously. The solution is boiled to expel nitrous fumes, further 20 ml.  $\text{HNO}_3$ ,  $d = 1.33$  are added, and the liquid is diluted to 100 ml., the lead peroxide being deposited on the electrode, after making it the anode, with a current of 2 amp. The tin is calculated by difference.

When the amount of lead is small, it may escape deposition. It appears that in the presence of hydrogen and stannic fluorides a catalytic influence is necessary to effect the deposition of the lead as peroxide, such an influence being exerted by the lead peroxide itself. For this reason, when the amount of lead is less than 0.060 gm. per 100 ml. solution, tin up to about 0.3 gm. being present, a known quantity of a standard solution of lead nitrate is added to the solution undergoing analysis in order to bring the lead concentration to the required value. This will cause the formation of a deposit of lead peroxide on the anode, capable by catalytic action of effecting the deposition of the remainder. The amount of lead added is, of course, deducted from the result.

## Separation of Cadmium from the Baser Metals.

### *Cadmium from Nickel or Cobalt.*

The fact that nickel and cobalt are more difficult to separate from acid solution than would be expected from their normal equilibrium potentials has already been commented upon. According to Lassieur, when a solution is electrolysed which contains cadmium, nickel and cobalt, and to which 3 ml. concentrated sulphuric acid per 125 ml. water have been added, only the cadmium is deposited. According to Böttger,

however, the separation does not yield trustworthy results. No doubt control of the cathode potential, and possibly preliminary coating of the electrode with cadmium, is necessary.

The study of the separation of cadmium from nickel and cobalt, as well as from iron, in cyanide solution, deserves attention.

### *Cadmium from Zinc.*

For the separation of cadmium from zinc we give the following *Examples*:

#### *Separation in HCl solution.*

Lassieur's electrodes. The original electrolyte contained about 0.3 gm. cadmium, 0.5 gm. zinc, 15 ml. concentrated HCl, and 1 gm. hydroxylamine hydrochloride in 150 ml. A little thymol blue was added, and the solution was then made alkaline with sodium hydroxide until the indicator showed a yellow colour. The solution was then again acidified with HCl until a cherry red colour had made its appearance; the volume was now 200 ml. Temperature ordinary. Initial current 1 amp. The uncorrected P.D. auxiliary N/1 calomel electrode-cathode is given as 0.65 volt. (Probable corrected P.D. about 0.8 volt.)

For the determination of the zinc remaining in the solution the latter was made alkaline to methyl red, and then 1 gm. KCN and 20 ml. 20 per cent  $\text{NH}_4\text{OH}$  solution were added. The liquid was concentrated to 150 ml. and the zinc deposited with a current of 3 amp.

#### *Separation in Acetate Solution.*

The separation may be carried out according to the prescription given on p. 78 for the deposition of cadmium.

#### *Separation in $\text{H}_2\text{SO}_4$ Solution.*

(W. D. Treadwell and K. S. Guiterman, *Zeit. anal. Chem.*, 1913.) Dish or crucible cathode. The metals are present as sulphates, other anions should be absent, 5 gm.  $\text{KHSO}_4$  are added. Temperature ordinary. Volts anode-cathode 2.6. Time 60 min. for 0.2 gm. cadmium. The method is suitable for the separation of cadmium from a fifty-fold quantity of zinc.

## Iron

The difficulty arising from residual currents when metals nobler than iron are deposited from solutions of this metal has been repeatedly referred to. For small quantities of iron this difficulty, due to the ordinary anode, may be circumvented by the addition of hydrazine or of hydroxylamine salts. When large quantities of iron are present, it is, however, better to use the reducing agents in conjunction with the diaphragm anode described on p. 26, fig. 19 (see J. G. Fife and S. Torrance, *Analyst*, 1937, 62, 29).

As already stated, the further study of the use of potassium cyanide for the separation of iron from its neighbours in the electro-potential series, cadmium and zinc, deserves attention.

The deposition of iron from ammonium oxalate solution (p. 79) has been advocated by Classen as a means of separating it from aluminium, chromium and manganese.

## Nickel and Cobalt

### *Nickel from Zinc.*

The separation of nickel from zinc in a hot ammoniacal solution containing conductance salts was proposed by v. Foregger in 1896. The method was improved by Hollard and Bertiaux by the addition of ammonium sulphite, which acts as a depolarizer at the anode. The method was further improved by A. Fischer, who controlled the potential of the cathode.

*Example.*—Fischer electrodes. The electrolyte contained about 0.15 gm. each of nickel and of zinc as sulphates. To this were added 6 gm.  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; 1 gm.  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ ; 30 ml.  $\text{NH}_4\text{OH}$   $d = 0.91$ . Volume of electrolyte 300 ml. Temperature about  $90^\circ$ . Current 1 to 0.3 amp. P.D.  $2\text{N} \cdot \text{H}_2\text{SO}_4$ ,  $\text{Hg}_2\text{SO}_4$  electrode-cathode 1.35 volt, i.e. for the saturated calomel electrode 0.95 volt. Time 20 minutes.

For the determination of the zinc Fischer recommends oxidation of the remaining sulphite by means of a few drops of

hydrogen peroxide, then concentration of the solution to about 250 ml., accompanied by expulsion of the greater part of the free ammonia. After this 6 to 8 gm. NaOH and 2 to 3 gm. tartaric acid are added. The solution is cooled to ordinary temperature, and the zinc is deposited with a current of 2.5 to 3 amp. in 45 min.

According to Lassieur, the solution from which the nickel has been removed may be employed without further preparation for the determination of the zinc. After cooling to ordinary temperature, the deposition may be effected within 30 min. by means of a current of 2 amp.

#### *Cobalt from Zinc.*

The method just given for the separation of nickel from zinc has hitherto been found inapplicable to cobalt. It might be worth while to test whether the employment of the parchment diaphragm anode would make a similar separation possible for cobalt.

#### *Nickel from Cobalt.*

Owing to the proximity of the deposition potentials of nickel and cobalt the separation of the two elements in the form of metal appears out of the question. As already stated, S. Torrance has, however, recently (*Analyst*, 1939, **64**, 109) elaborated a method which is based on the suggestion originally made by Coehn and Gläser (p. 75) to deposit the cobalt on the anode as  $\text{Co}_2\text{O}_3$ . Torrance uses the writer's diaphragm revolving electrode as the cathode. The maximum amount of cobalt which was successfully deposited was about 0.04 gm., the maximum amount of nickel present at the same time being about 1 gm. The deposited cobaltic oxide contains a little nickel and must therefore be dissolved and redeposited, after which it is found to be pure. The  $p_{\text{H}}$  of the solution should be about 5, and as it tends to become more acid during a determination owing to the entrance of mineral acid from the cathode chamber, it must be well buffered. To produce a firm adherent deposit a high temperature is necessary.

*Example.*—To the solution containing the nickel and cobalt 1 ml. glacial acetic acid and 10 gm. sodium acetate are added and made up to about 100 ml. Cathode: revolving diaphragm electrode, catholyte 2N nitric acid, anode new pattern gauze electrode. Temperature 90° to 95° C. Current 0.5 amp. for 10 min., after which the catholyte is flushed into the anolyte by introducing through the funnel of the electrode another 5 ml. 2N nitric acid. The current is then increased to 1 amp., the catholyte is again flushed into the anolyte after another 10 min., and electrolysis continued for another 10 min., thus making the total time 30 min. The deposit is then washed and dissolved by warming the electrode with 20 ml. 2N nitric acid to which two drops of sulphurous acid solution are added. The nitrate solution is evaporated to dryness, the last stages being carried out over a water bath. The salt left is then taken up in water, and the solution buffered with acetic acid and sodium acetate as before. The electrolysis is repeated as detailed above, the oxide washed and dried in alcohol and ether in the usual way. The cobaltic oxide is weighed and the theoretical factor of 0.71 applied to find the weight of metallic cobalt. If desired, the oxide may be dissolved and the cobalt deposited as metal. For this purpose the oxide is dissolved in 20 ml. warm 20 per cent sulphuric acid to which a few drops of sulphurous acid are added. The excess sulphurous acid is boiled off, the solution is made strongly ammoniacal and the metal deposited from it according to one of the prescriptions given on p. 76.

## Zinc

The separation of zinc from the nobler metals has been discussed. In the deposition of zinc the most negative electrode potential obtainable is always employed. The question thus arises whether any of the metals which are not reduced electrolytically in aqueous solution on solid cathodes may be precipitated along with zinc in traces either as hydroxide or in the state of alloy.

From the available data it appears that when the prescriptions given for the deposition of zinc are followed, zinc may be separated quantitatively from most of the more electro-

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positive metals. Thus experiments by W. J. Grant in the writer's laboratory have shown that with the Paweck electrode zinc may be separated quantitatively from aluminium in acetic acid solution. When large quantities of magnesium salts were present, slightly high results were found, and reprecipitation of the zinc after solution in sulphuric acid and reconstitution of the acetate electrolyte were necessary.

Zinc may also be separated from metals such as iron, which form very stable double cyanides, by depositing it from a cyanide bath; and similarly it may be separated from metals such as nickel that form very stable complex tartrates by depositing it from an alkaline tartrate bath.

*Example* (J. H. Buckminster and E. F. Smith, *J. Amer. Chem. Soc.*, 1910, **32**, 1471).—Revolving crucible cathode or the writer's modified electrodes. The solution contains about 0.15 gm. Zn and 0.15 gm. Ni as sulphate. To this is added 1 gm. Rochelle salt and sufficient KOH to redissolve the hydroxides first precipitated. Current about 0.3 amp., P.D. anode-cathode about 2.4 volt. Temperature ordinary. Time 45 min.



## CHAPTER V

### APPLICATIONS TO THE ANALYSIS OF INDUSTRIAL ALLOYS

#### *Example 1. The Analysis of Yellow Metal Alloys.*

The alloys to be considered comprise the ordinary brasses and bronzes, in which the metals copper, lead, tin and zinc may be separated and determined by electro-deposition. Chloride solutions containing a small amount of nitric acid are employed, the copper being determined first (p. 62); the lead and tin are deposited together and then redissolved and separated according to the example given on p. 94. The zinc finally is deposited from alkaline solution after converting it into the cyanide complex. Traces of iron or phosphorus are determined by the usual non-electrolytic methods. For the theory of the separation of arsenic, when present, see p. 92.

For brasses containing only very small amounts of tin a method differing from the one to be described may be employed. In this the alloy is dissolved in nitric acid, the tin being weighed as dioxide. The lead is deposited as peroxide from a strongly acid nitrate solution. After evaporating to fumes with a suitable amount of sulphuric acid, the copper is determined, preferably with control of the cathode potential. The iron is precipitated with ammonium hydroxide, and the zinc determined in the residual solution by depositing it on the Paweck cathode after converting it into the acetate (p. 82, *Example 1*). This method will be found to require more time than the one first indicated. The latter is due to Lassieur and has been further developed by S. Torrance (*Analyst*, 1937, 62, 721).

0.2 to 0.4 gm. alloy is dissolved in a mixture of 10 ml. HCl (1.16), 2 ml.  $\text{HNO}_3$  (1.42), 10 ml.  $\text{H}_2\text{O}$ , and 1 gm.  $\text{NH}_4\text{Cl}$ . After solution 5 ml. HCl are added, and the liquid is diluted to 150 ml. One gram hydrazine hydrochloride is then added. Writer's modified electrodes. P.D. saturated calomel electrode-cathode, confined to 0.40 volt. The initial current is 3 to 4 amp., but falls rapidly to about 0.1 amp. Temperature  $50^\circ$ . Time 20 min. All the copper is deposited, together with any arsenic that may be present. In such a case, it is necessary to dissolve the deposit in a mixture of 5 ml.  $\text{H}_2\text{SO}_4$  (1.82), 5 ml.  $\text{HNO}_3$  (1.42) and 10 ml.  $\text{H}_2\text{O}$ . Oxides of nitrogen are boiled off, the solution is diluted to 150 ml., and electrolysed at an auxiliary potential of 0.4 volt at room temperature. Copper alone is deposited.

One gram hydrazine hydrochloride is then added to the original residual solution, and the tin and lead are deposited together at ordinary temperature, the P.D. saturated calomel electrode-cathode being limited to 0.7 volt. The deposit containing the two metals is weighed, and the lead separated as peroxide as follows. The deposit is dissolved in a mixture of 15 ml.  $\text{HNO}_3$  (1.42), 5 ml. HF (conc.), and 15 ml. water, oxides of nitrogen being boiled off. Low-lead alloys will contain insufficient lead for deposition from nitric-hydrofluoric acid solution as lead peroxide. In the case of such alloys, 20 ml. of a standard 0.5 per cent solution of lead as lead nitrate are added, the mixture is diluted to 150 ml., and electrolysed with a current of 6 to 6.5 amp. for 20 min. at a temperature of  $90$  to  $95^\circ\text{C}$ . The deposit of lead peroxide is weighed, the amount of lead in it calculated, and the weight of lead which was added as nitrate deducted. The weight of tin is obtained by difference.

The solution left after the removal of the tin and the lead is oxidized by boiling with a little bromine till colourless. Concentrated ammonium hydroxide solution is added until the solution is just pink to phenolphthalein, and washed. The iron may be determined by dissolving the precipitate in HCl and estimating colorimetrically with thiocyanate. (F. Sutton, *Volumetric Analysis*, 12th edn., London, 1935, p. 265.) Before the deposition of the zinc 10 ml. concentrated ammonium hydroxide, and 10 ml. 10 per cent potassium cyanide solution are added to the filtrate. The latter is cooled and electrolysed with a current of 3 amp. for 20 min. at room temperature.

The following numbers afford a comparison in the case of a bronze between results obtained by electrolysis and those obtained by standard chemical methods in the laboratories of the L.N.E.R. at Stratford. For the electrolytic analyses, 0.2500 gm. alloy was taken in every instance:

	L.N.E.R. Laboratory	By Electrolytic Method		
		1	2	3
Copper ..	84.6%	84.4	84.5	84.6
Lead .. ..	3.8%	3.8	3.8	3.7
Tin .. ..	6.9%	7.0	7.0	6.9
Zinc .. ..	4.4%	4.5	4.4	4.4

*Example 2. The Analysis of White Metal Alloys.*

These alloys contain antimony in addition to the constituents considered in the case of the yellow metal alloys. The general procedure is similar to that discussed for the last-named alloys; the antimony and copper are, however, deposited together, and then separated as described in the example given on p. 91. The following instructions, based on the work of Lassieur, have been given by S. Torrance (*Analyst*, 1937, 62, 719).

0.2 to 0.4 gm. alloy as drillings or sawings is weighed into a beaker. It may be found convenient to weigh the alloy into one of a pair of balanced copper pans. The alloy is dissolved by warming with a mixture of 10 ml. hydrochloric acid (1.16) and 10 ml. distilled water, a gram of ammonium chloride being added to minimize loss of tin as stannic chloride. Complete solution may be hastened by the addition, drop by drop, of a saturated solution of potassium chlorate. When all the alloy is dissolved and excess chlorine boiled off, 5 ml. hydrochloric acid are added, and the solution is diluted to 150 ml. and 1 gm. hydrazine hydrochloride is added. The liquid is electrolysed with the writer's modified electrodes at a P.D. saturated calomel electrode-cathode of 0.4 volt, and at a temperature of 70° to 75° C. The copper and the antimony are deposited together. The fluctuations of current due to the reduction of stannic to stan-

nous ions in the presence of antimony (p. 89) are observed. After 15 to 20 min. the current is reduced to a minimum. The liquid in the tip of the auxiliary electrode vessel is flushed out into the electrolysis beaker, and the electrolysis continued for a further 5 to 10 min., after which the copper-antimony deposit is dried and weighed. The separation of the copper from the antimony is effected by dissolving the deposit in a mixture of 5 ml.  $\text{HNO}_3$  ( $d = 1.42$ ), 5 ml. 40 per cent HF, and 10 ml.  $\text{H}_2\text{O}$ , boiling off oxides of nitrogen, diluting to 150 ml., adding a solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , drop by drop, until the liquid is distinctly yellow, and depositing the copper by electrolysis at a P.D. auxiliary saturated calomel electrode-cathode of 0.4 volt at room temperature for 20 min. The weight of antimony is obtained by difference.

The tin and lead are deposited together, after adding 1 gm. of hydrazine hydrochloride to the original residual solution by electrolysis at an auxiliary potential of 0.7 volt for 20 min. at room temperature. As already described for the yellow metal alloys, the deposit is dissolved in a mixture of 15 ml.  $\text{HNO}_3$ , 5 ml. HF (conc.) and 15 ml. water, oxides of nitrogen being boiled off. Here again, in the case of low-lead alloys there will be insufficient lead present for deposition as peroxide from hydrofluoric acid solutions. In such cases as described for the yellow metal alloys 20 ml. of a 0.5 per cent standard solution of lead as lead nitrate are added. High-lead alloys containing over 25 per cent lead do not require any such addition. The liquid is diluted to 150 ml. and electrolysed with a current of 6 to 6.5 amp. for 20 min. at a temperature of  $90^\circ$  to  $95^\circ \text{C.}$ , as in the case of the yellow metal alloys. We give here comparison results obtained by S. Torrance for high- and low-lead white metal alloys. The weight of alloy taken was in every case 0.25 gm.

	Carriage and Wagon White Metal (Old)			
	L.N.E.R. Laboratory	By Electrolytic Method		
		1	2	3
Antimony	11.9%	12.0	11.9	11.9
Copper ..	2.7%	2.7	2.7	2.7
Lead ..	34.0%	34.2	34.2	34.2
Tin ..	51.4%	51.1	51.2	51.1

	Locomotive White Metal (Old)				
	L.N.E.R. Laboratory	By Electrolytic Method			
		1	2	3	4
Antimony ..	9.6%	9.6	9.6	8.5	9.6
Copper ..	6.0%	6.0	6.0	6.0	6.0
Lead ..	5.1%	5.0	5.2	5.0	5.1
Tin ..	79.3%	79.2	79.0	79.2	79.1

*Example 3. The Analysis of Nickel Bronzes* (alloys of copper, tin, lead, zinc and nickel, together with small amounts of iron, aluminium and manganese).

The following directions are taken from a paper by S. Torrance (*Analyst*, 1938, **63**, 488).—From 0.5 to 1.0 gm. of the alloy, in the form of fine sawings or drillings, are heated with 10 ml. of hydrochloric acid ( $d = 1.16$ ) and 1 gm. of ammonium chloride, the latter being added to minimize loss of tin as stannic chloride. Complete solution is effected by the addition, drop by drop, of a saturated solution of potassium chlorate, with boiling after each addition. The solution is then evaporated down in order to decompose excess of chlorate, and diluted to 100 ml., and 5 ml. hydrochloric acid and 1 gm. hydrazine hydrochloride are added. Copper is deposited by electrolysis the solution at  $50^{\circ}\text{C}$ ., at a cathode potential to the saturated calomel electrode of  $-0.4$  volt. The current falls rapidly almost to zero, and reaches a minimum after about 10 min. After further 5 min. the liquid in the tip of the auxiliary electrode is flushed out into the electrolysis vessel, and the electrolysis is continued for 5 min. more. Tin and lead are next deposited together as follows. The solution is cooled to room temperature, and electrolysed for 20 min. at  $20^{\circ}\text{C}$ ., with a cathode potential of  $-0.7$  volt. The tin and lead are weighed together, dissolved in nitric, hydrofluoric acid mixture, and the lead is determined as peroxide according to the example given on p. 94. The residual solution from the tin plus lead is evaporated with 5 ml. sulphuric acid ( $d = 1.82$ ) until fumes appear, and then taken up in 50 ml. of water, and ammonia is added until the liquid is just alkaline to phenolphthalein. The mixture is boiled, and the hydroxides of iron

and aluminium are filtered off and thoroughly washed with hot water. The iron is separated from the aluminium by boiling the precipitate with a little sodium peroxide and water, and refiltering the undissolved iron, which is determined gravimetrically, volumetrically, or if present only in traces, colorimetrically. (F. Sutton, *Volumetric Analysis* (12th Ed., London, 1935), p. 265.) The aluminium is determined colorimetrically by the use of aluminon. (Hopkin and Williams, *Organic Reagents for Metals* (3rd Ed., London, 1938), p. 15).

Twenty millilitres of ammonia solution ( $d = 0.880$ ) in excess and 2 gm. of sodium sulphite are added to the filtrate, and nickel is deposited by electrolysis for 20 min., at  $70^{\circ}\text{C.}$ , with a cathode potential of  $-1.0$  to  $-1.1$  volt. The solution is cooled to room temperature, 5 ml. of ammonia solution are added, and the zinc is deposited by electrolysis the solution for 30 min. at  $20^{\circ}\text{C.}$ , with a current of 3 amp. The residual solution is heated to boiling, and any manganese present is precipitated as the sulphide by passing hydrogen sulphide gas for 5 to 10 min. The precipitate is filtered off, washed with water saturated with hydrogen sulphide, dissolved in a little nitric acid and oxidized to permanganate with some sodium bismuthate. This permanganate is determined colorimetrically, or, if the amount of manganese warrant, volumetrically. (F. Sutton, *op. cit.*, p. 67.)

*Example 4. The Analysis of Light Aluminium Alloys* (alloys of aluminium, copper, zinc, nickel and silicon, together with iron, tin, lead, manganese and magnesium).

Of the metals contained in light aluminium alloys copper, lead, tin, nickel and zinc may be estimated electrolytically. In the determination of nickel and zinc a difficulty arises from the formation of a bulky precipitate of aluminium hydroxide in the ammoniacal solution recommended on p. 76. This cannot simply be removed by filtration, since it absorbs nickel and zinc ions. The difficulty was overcome by Torrance by the addition of tartaric acid to keep the aluminium hydroxide in solution. The following instructions are given (*Analyst*, 1938, 63, 489).

From 0.5 to 1.0 gm. of the alloy is dissolved in a mixture of 10 ml. of hydrochloric acid ( $d = 1.16$ ) and 20 ml. of water in

a covered beaker, the mixture being gently warmed if necessary. When effervescence ceases the black residue is taken up by boiling with 2 to 3 drops of a saturated solution of potassium chlorate, and excess of chlorine is boiled off. The solution is cooled, 15 ml. of sulphuric acid ( $d = 1.82$ ) are added, and the mixture is evaporated very carefully until fumes appear, after which the heating is continued for 5 to 10 min., care being taken to avoid baking. The residue is then cooled, taken up in 50 ml. of water and 10 ml. of hydrochloric acid, and boiled until the mixed sulphates are dissolved. The silica thus precipitated is filtered off from the hot liquid, washed with hot dilute acid and ignited, and finally determined by heating with hydrofluoric acid and sulphuric acid. If the alloy contains more than about 5 per cent of lead, the lead sulphate may not be completely soluble in the hydrochloric acid, and some may be filtered off with the silica. The residue from the hydrofluoric acid treatment is dissolved in nitric acid, and the lead is deposited as peroxide electrolytically (p. 74). One gram of hydrazine hydrochloride is added to the filtrate, which is electrolysed for 20 min. at  $50^{\circ}\text{C}$ . The cathode-saturated calomel electrode potential is maintained at  $-0.4$  volt and the copper separates out. Tin and lead are next deposited together by increasing the potential of the auxiliary electrode to  $0.7$  volt, the temperature being  $20^{\circ}\text{C}$ ., and the time 15 to 20 min. The lead is separated as indicated in the example given on p. 94.

From 5 to 10 gm. of tartaric acid are added to the residual solution, which is made just alkaline with ammonia, 20 ml. of ammonia solution ( $d = 0.880$ ) in excess and 2 gm. of sodium sulphite are added, and the mixture is electrolysed for 20 min. at  $70^{\circ}\text{C}$ . to deposit the nickel, the cathode potential being  $-1.0$  to  $-1.1$  volt. The solution is cooled to  $20^{\circ}\text{C}$ ., 5 ml. of ammonia solution are added, and the zinc is deposited by electrolysing for 25 to 30 min. at  $20^{\circ}\text{C}$ ., with a current of 3 amp.

The residual solution is heated to boiling, and hydrogen sulphide gas is passed for 10 min. The iron and manganese are precipitated as sulphides, filtered off, washed well with water saturated with hydrogen sulphide, and dissolved in nitric acid. The solution is boiled to oxidize the iron, which is precipitated by the addition of ammonia. The precipitate

is filtered off, and may be determined by one of the methods mentioned in the previous example. The manganese is determined by acidifying and oxidizing with bismuthate. The filtrate from the sulphide separation is boiled with 10 gm. of caustic soda, to expel hydrogen sulphide and ammonia. Since aluminium is not precipitated by 8-hydroxyquinoline from a caustic tartrate solution, the magnesium is determined by adding 8-hydroxyquinoline. (Hopkins and Williams, *Organic Reagents for Metals*, p. 67.) Aluminium is determined by difference.

If the nickel contains cobalt which it is desired to determine, the deposit of nickel is weighed and then dissolved in 20 ml. of 20 per cent nitric acid. The solution is evaporated to dryness, the mixed nitrates are taken up in water, and the cobalt is determined as oxide, as described on p. 98. The nickel is found by difference.

*Example 5. The Determination of Bismuth in Fusible Alloys.*

The determination of bismuth in bismuth-, tin-, lead alloys is a matter of importance. The following particulars are due to F. G. Kny-Jones (*Analyst*, 1939, 24, 172).

About 0.4 to 0.5 gm. of drillings are attacked with 1 to 2 ml. of concentrated nitric acid. After the reaction has subsided in violence, 10 ml. of concentrated hydrochloric acid are added, and the resulting solution is boiled. After the addition of further 5 ml. of concentrated hydrochloric acid, the solution is diluted to 100 ml. with water, 5 gm. of oxalic acid and 0.5 gm. of hydrazine hydrochloride are added, and the solution is heated to 80 to 85°C. The electrolysis is then carried out as described on p. 64, the P.D. saturated calomel electrode-cathode being 0.15 to 0.17 volt, which is taken in steps of about 0.02 volt to a final value of 0.25 to 0.30 volt, the initial current varying in different determinations from 0.25 to 0.4 amp. Time about 30 min.



## CHAPTER VI

### INTERNAL ELECTROLYSIS

The use in galvanoplastics and electroplating of the methods, to which the writer has applied the general term of "Internal Electrolysis", dates from before 1840. In these methods the electric current, which is employed usefully in effecting electro-deposition, is generated in the deposition cell itself. The first application of this principle to electrolytic analysis appears to be due to C. Ullgren (*Z. anal. Chem.*, 1868, 7, 442), who recorded experiments in which copper was determined by deposition from a sulphate solution. The general principles which underlie the application of this method of analysis to the separation of metals from each other, were enunciated by Hollard and Bertiaux (*Bull. Soc. Chim.*, 1903, 29, 116, and 1904, 31, 102; and *Analyse des Métaux par Electrolyse*, Paris, 1906, pp. 24 and 99). The last-named authors were successful particularly in the separation of nickel from zinc. The application of the method particularly to the rapid separation of small quantities of a nobler metal from large quantities of a baser one with simultaneous vigorous stirring was rendered possible by the apparatus described by the writer in 1930 (*Analyst*, 1930, 55, 309).

The apparatus comprises one or two anodes of the baser metal, each placed in a compartment, which is separated from the test solution by a parchment diaphragm. There are also a platinum gauze cathode which is connected externally to the anodes and a stirrer of the centrifugal type. The apparatus is explained in figs. 1 and 2, the former representing the design originally used, while the latter explains some recent modifications. In both forms the apparatus is built up on a circular wooden lid L, the components being held

in suitably arranged holes. With anodes having shoulders below the lid, as shown in fig. 1, it is necessary to make the lid divisible into halves which are held together by dowels and hooks. When brittle metals such as bismuth are employed as anodes it is necessary to cast them as hollow cylinders such as those shown in fig. 1 at A. Metals which are obtainable

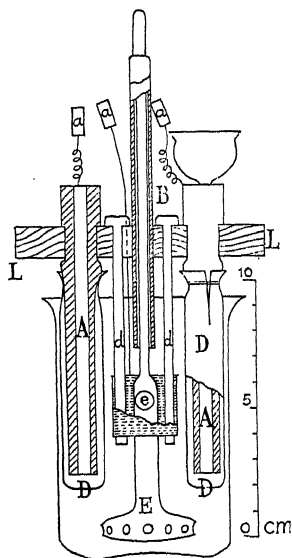


Fig. 1.—Apparatus for Internal Electrolysis

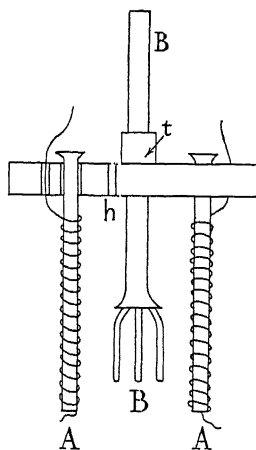


Fig. 2.—Modifications of Apparatus of fig. 1

as wire or as foil are, however, more conveniently wound round glass tubes, as shown at A in fig. 2. Around the anodes the diaphragms D are disposed as shown in fig. 1. These are prepared from Whatman diffusion shells of 16 mm. diameter. After softening in water they are cut to the proper length and provided with slots cut lengthwise at the top. They are then tied into position by means of thread or by rubber bands. The anode compartments may be filled with indifferent electrolyte through their tubes by means of a

pipette or by a funnel such as that shown in fig. 1. If desired, their contents may be washed into the outer vessel by the addition of further electrolyte towards the end of a determination. In the applications we are considering this procedure was, however, found unnecessary. The cathode is shown in fig. 1. It is a platinum gauze cylinder of 2.6 cm. diameter and 2.5 cm. height. Its leading-in wire of about 1 mm. diameter and about 12 cm. length is attached to the bottom and tied to the top, as described on p. 23. The cathode may be held in position by means of a tripod such as that shown at B in fig. 2. This is analogous to the tripods used with the writer's modified electrodes. In the present application the cathode is pulled over the tripod's legs. The tube B serves as a guide to the stirrer, and is hindered from falling out of the lid when not in use by the ring of rubber tubing shown at *t* in fig. 2. In fig. 1 the cathode is shown held by independent glass rods *d* fitted into the lid. J. G. Fife uses as a support for the cathode a wide glass tube which is attached to the guide tube by a cork ring and just fits into the cathode.

The centrifugal stirrer shown at E in fig. 1 comprises a lenticular bulb of 3.7 cm. diameter, fitted with twelve holes and a stem, the lower portion of which is hollow to a height of 4 to 6 cm. This portion is of about 1.4 cm. external diameter and has two holes *e* of about 8 mm. opposite each other at the top. The stem of the stirrer is of about 6 mm. diameter. It revolves inside the guide tube B, and is drawn down at the top to fit a rubber tube or other flexible connexion to the driving shaft.

The stand may be improvised from laboratory fittings, or where available, one of the writer's electrolytic stands may be employed. A heavy stand is necessary to which a retort ring for supporting the lid is clamped. This must also be done when the electrolytic stand is employed. The beaker is either supported by a tripod which can be removed from below it at the end of a determination, or more conveniently by the sliding support of the electrolytic stand. When using the latter the stirrer is held by the inner electrode clutch. Where a special motor has to be fitted, this may be done

conveniently by placing it with its shaft vertically above the stirrer to which it is connected by a piece of thick-walled rubber tubing. The motor may be protected from vapours rising from the beaker by means of a uralite plate. The two anodes and the cathode must be connected by wires having no appreciable resistance. These wires connected to tabs *a* are shown in fig. 1 above. Originally a laboratory clamp was employed for holding the guide tube of the stirrer and at the same time clamping the three tabs of the electrodes together. Latterly the tabs have been omitted, the anode wires have been soldered to the clamp and connexion to the cathode wire has been made by the clamp itself, the cork lining on its fixed jaw having been removed. Where the clamp shown in fig. 26 (p. 33) is used, connexion to the anode wires is made by the double terminal provided, the cathode leading-in wire being held in the usual way by the silver-lined jaw. A photographic illustration of an improvised stand is given in the *Analyst* of 1930, p. 310.

#### *Method of Working.*

The beaker support is lowered and the weighed cathode placed in position from below, the leading-in wire being pushed through the hole *h*, fig. 2, and then clamped on to the glass guide-tube as explained. The stirrer is then inserted, and the beaker of about 400 ml. capacity with its solution, usually about 250 ml., is placed in position from below. For disconnecting, the stirrer is stopped, the beaker support is lowered or otherwise removed, and the cathode washed as in ordinary electrolytic analysis. The stirrer and the cathode are then removed, the latter being dried in the usual way after washing in alcohol and ether or in acetone.

#### *Method of J. J. Lurie and L. B. Ginsburg.*

J. J. Lurie and L. B. Ginsburg (*Ind. Eng. Chem. (Anal.)*, 1937, 9, 424, where further references are given) have carried out determinations of metals more noble than lead by means of internal electrolysis. They employ an apparatus without stirrer and without diaphragm. It is stated that the chemical

action of the lead anode on the copper and bismuth ions contained in the solution is practically nil. It appears to the present writer that the dependence on natural convection currents in the test solution and the possibility of cementation must be a cause for uncertainty when the experimental conditions are slightly departed from.

### *Theoretical Considerations and Applications.*

As will be seen from the following examples, the main usefulness of the method of internal electrolysis lies in the fact that it affords a method for the separation of a nobler metal from a baser one, the potential of the cathode being automatically controlled in the simplest possible manner. The fact that an external source of current is not required is only a secondary consideration. As already explained, the anode consists of the metal which is to remain in solution; all nobler metals will thus deposit on the cathode. In order that no conditions may arise under which the anode metal might also deposit, the concentration of its ions should always be maintained slightly higher in the anode than in the cathode compartment. The E.M.F. available in internal electrolysis cells is always small, and it is thus imperative that the electrolyte should be chosen in such a way that no solution of the deposited metal can take place owing to the action of air or other oxidizing agent. This is usually achieved by the addition of hydrazine or hydroxylamine salts or of other reducing agents. In the determination of metals more base than hydrogen, the  $p_H$  of the electrolyte must always be high enough to prevent liberation of hydrogen in preference to deposition of the metal. It is very important that no transfer-resistances should develop, particularly on the anodes, and therefore compounds which are as soluble as possible should always be employed. Thus, in the separation of traces of cadmium from zinc, it was found necessary to use ammine chlorides instead of sulphates (J. G. Fife, *Analyst*, 1936, **61**, 681). In all electrolytes the temperature is maintained high—usually at about 70° C.—the liquid having been heated before being placed in position for electrolysis. This will

tend to improve the quality of the deposit, the conductivity of the electrolyte, and the reducing efficiency of the depolarizer added. The current strength in internal electrolysis experiments usually starts at values varying between about 0.1 amp. and 0.03 amp. At the close of an experiment it becomes very small. The time required for a deposition should be determined by taking the deposit to constant weight, or preferably by blank experiments. Once determined under given conditions in a particular case, a suitable value may safely be adopted in repeat experiments.

We give the following applications:

#### **Determination of Small Quantities of Silver in Galena and in Pyrites (Fife, *Analyst*, 1937, 62, 723).**

The determinations to be described are based on the following three separations:

(a) *Separation of small quantities of Silver in the presence of large quantities of Lead, and small quantities of Copper and Bismuth in nitric acid solution.*

As stated on p. 54, silver tends to form loose crystals when deposited from nitric acid solution; the upper limit given for its determination by means of the present apparatus is 8.5 mgm. Enough nitric acid to prevent the formation of basic bismuth salts must always be present.

*Example.*—Catholyte to be analysed: Lead nitrate equivalent to 10 gm. Pb; Copper, maximum, 0.03 gm.; Bismuth, maximum 0.02 gm.; Free nitric acid ( $d = 1.42$ ), 9 ml.

Anolyte: Copper nitrate corresponding to 1 gm. Cu,  $\text{HNO}_3$  ( $d = 1.42$ ), 0.1 ml. per 100 ml. Anode: Copper wire of 18 S.W.G. Temperature about 60° C. Time 30 min.

(b) *Separation of small quantities of Silver from small quantities of Copper in ammoniacal solution.*

Since the cupric ammine complex interacts both with silver and with copper with the production of the corresponding cuprous ammine complex, it is necessary that all copper in

the catholyte should be in the cuprous condition. In the anolyte, however, it was found that the development of transfer resistances was avoided only by the employment of cupric solutions in the presence of ammonium salts. These facts explain the following instructions.

*Example.*—The catholyte to be analysed was made up of 7 gm. sodium sulphite, 9 ml. ammonium hydroxide ( $d = 0.88$ ), to which quantities of copper and silver nitrate were added corresponding to about 20 mgm. Cu and 10 mgm. Ag. Volume about 300 ml. The solution was heated a short time before electrolysis, until it was colourless. Anolyte: 0.1 gm. Cu, added as  $\text{Cu}(\text{NO}_3)_2$ , 2 gm.  $\text{NH}_4\text{NO}_3$ , 3 ml.  $\text{NH}_4\text{OH}$  solution ( $d = 0.88$ ) per 100 ml. Anode: Copper wire of 18 S.W.G. It is recommended to wash the anodes with nitric acid after every second experiment at least, since a tendency to form badly conducting black deposits was found. Temperature about  $70^\circ \text{C}$ . Time for quantities of silver up to 5 mgm. about 30 min., for quantities up to 10 mgm. 50 min.

(c) *Separation of small quantities of Silver from large quantities of Copper and Iron, and small quantities of Nickel, Arsenic and Zinc in sulphuric acid solution.*

As will be understood, the iron must be in the ferrous condition. This can be readily ensured by the addition of hydrazine sulphate.

*Example.*—The catholyte contained about 5 gm. copper and 5 gm. iron as sulphate, about 10 ml. concentrated sulphuric acid, 0.4 gm. hydrazine sulphate, and about 10 mgm. nickel, up to 50 mgm. arsenic and zinc, and from 1 to 10 mgm. silver in about 300 ml. Anolyte: Copper sulphate equivalent to 5 gm. Cu and 0.1 ml. concentrated sulphuric acid per 100 ml. solution. Anode: Copper wire of 18 S.W.G. Temperature about  $60^\circ \text{C}$ . Time about 30 minutes.

*Silver in Galena*

From 15 to 20 gm. of mineral is treated with nitric acid (1 part concentrated acid to 10 parts of water) and boiled for about 30 min., an excess corresponding to about 9 ml. concentrated acid being used. The solution is filtered, the filtrate diluted to about 300 ml. and subjected to internal electrolysis for the determination of silver, as detailed above under (a) for nitrate solutions.

The greater part of the silver is, however, usually left in the residue, possibly as chloride, and is extracted at room temperature for an hour with intermittent stirring with 30 ml. of 10 per cent potassium cyanide solution and about 60 ml. of water. The liquid is filtered, the filtrate acidified with nitric acid, and boiled to remove all hydrocyanic acid. Care must be exercised to expel all the hydrogen cyanide, since any cyanide left would subsequently make complete deposition of silver according to (b) impossible. The solution is then neutralized with ammonia, and a further 9 ml. of ammonia ( $d = 0.88$ ) and 7 gm. sodium sulphite are added. The solution is boiled for a short time, and filtered if necessary. The filtrate is then electrolysed internally according to the instructions given under (b), the silver found plus that determined from the nitrate solution representing the total silver in the galena. Results are adduced which are identical with those found by the usual fire assay method.

*Silver in Cupreous Iron Pyrites*

About 20 gm. pyrites are weighed out, and heated on a sand bath for about an hour with a solution of 20 ml. concentrated sulphuric acid in about 60 ml. water. The liquid is filtered, the residue washed, and 1 gm. hydrazine sulphate added to the filtrate, from which the silver is then deposited according to (c).

As with the galena, a large part of the silver is left in the residue from the acid extraction which must be treated in the identical manner with potassium cyanide solution that has been described under galena. Here, too, in the case of a cupreous iron pyrites containing 0.0047 per cent silver, a result identical with that found by the usual metallurgical method was obtained.



**Traces of Mercury in Brass.** (J. G. Fife, *Analyst*, 1938, 63, 650.)

Traces of mercury sometimes find their way into brass condenser tubes, and cause embrittlement. To detect and estimate such traces the method of internal electrolysis may, according to experiments of J. G. Fife, be usefully employed. Five grammes of the metal are converted into nitrate, evaporated to fumes with about 70 ml. 10 per cent sulphuric acid, diluted to 300 ml. and electrolysed in the internal electrolysis apparatus at a temperature of about 60° C. The ordinary platinum cathode is employed. The anode is a coil wound from 18 S.W.G. copper wire, the anolyte containing about 20 gm.  $\text{CuSO}_4$ ,  $5\text{H}_2\text{O}$  and 2 ml. conc.  $\text{H}_2\text{SO}_4$  per 100 ml. Amounts of mercury varying from about 0.5 to about 6 mgm. may be determined. Time 30 to 40 minutes.

**Determination of Small Quantities of Copper in Large Quantities of Iron.** (J. G. Fife and S. Torrance, *Analyst*, 1937, 62, 30.)

The electrolytic separation of copper from large quantities of iron has long been considered impracticable on account of the difficulties repeatedly referred to. These difficulties do not arise in the method of internal electrolysis, which readily allows the iron to be maintained in the ferrous state in the electrolyte. The solution must always contain enough sulphuric acid to keep it clear, and a small quantity of hydrazine sulphate is employed as the reducing agent.

*Example.*—The catholyte contained 5 gm. iron, added as ferrous sulphate, the copper varying from 1 to 30 mgm. in various experiments. There were added 0.2 gm. hydrazine sulphate, and 3 ml. 96 per cent sulphuric acid. Volume about 300 ml.

The anolyte contained ferrous sulphate equivalent to 5 gm. Fe, 3 ml. 96 per cent sulphuric acid, and 0.2 gm. hydrazine sulphate per 100 ml. Temperature about 70° C. Time about 30 min. Anode: iron wire of about 1 mm. diameter.

*Copper in Steels.*

About 3 to 10 gm. of the steel, according to the amount of copper present, is dissolved in sulphuric acid in an atmosphere of carbon dioxide, using, e.g. a Contat-Göckel valve (Treadwell and Hall, *Analytical Chemistry*, 8th Ed., Vol II, p. 549), the solution is cooled, filtered and neutralized with caustic soda or ammonia, and 3 ml. of 96 per cent sulphuric acid and sufficient hydrazine or hydroxylamine sulphate are added to convert any ferric into ferrous ions, and leave an excess. It is advisable to ensure the absence of ferric ions by testing with ammonium thiocyanate. The solution is then diluted to about 300 ml. and subjected to internal electrolysis as described above. The residue left after solution of the steel in sulphuric acid may be neglected, as special experiments showed that it contains no copper.

**Determination of Small Quantities of Bismuth and of Copper in the Presence of Small Quantities of Silver and of Antimony, and of Large Quantities of Lead.** (E. M. Collin, *Analyst*, 1930, **55**, 312 and 680.)

In the estimations to be recorded, the quantitative determination of the silver and the antimony by electrolysis is not considered. If desired, the silver may, however, be estimated electrolytically, as already described. According to the present prescription the silver is removed as chloride, and the antimony is kept in solution by the addition of tartaric acid, and prevented from electro-deposition by oxidation to the quinquevalent state with permanganate. The copper and bismuth are deposited together, then redissolved in nitric acid, and separated by means of ammonia and ammonium carbonate. From the solutions thus obtained the metals may be deposited individually in the internal electrolysis apparatus, or the combined metals may be weighed, and one of them determined by difference. In the present case it was found that for bismuth deposition the temperature of the electrolyte must not be below 85° to 90° C., probably on account of the chloride present in small quantity.

*Example 1. Determination of Bismuth and Copper in Lead Bullion.*

Five to ten grams of the sample are dissolved in 50 to 100 ml., 20 per cent nitric acid with the addition of 1 to 2 gm. tartaric acid. Two millilitres of 2 per cent hydrochloric acid are added, and the precipitate of silver chloride is allowed to coagulate at a gentle heat, and then filtered off together with any insoluble residue from the lead. The precipitate is washed well with hot water, and the filtrate diluted to about 100 ml. and cooled; then a 2 per cent permanganate solution is added as long as it is decolorized. Five ml. of a 5 per cent solution of hydroxylamine hydrochloride are added, and after dilution to about 200 ml. the solution is electrolysed in the internal electrolysis apparatus at a temperature of 85 to 90° C. for 15 min. The time given was found adequate for quantities of bismuth up to 8 mgm. Except in routine experiments, it is advisable to take the deposit to constant weight. In no case should the amount of bismuth exceed 10 mgm. on account of the somewhat loose nature of the deposit. There is no such limit to the amount of copper that may be present. The anode compartment contained a 5 per cent solution of lead nitrate acidified with nitric acid. Pure lead foil or wire is used as the anode.

In order to separate the bismuth from the copper the deposit is dissolved in a small amount of nitric acid (1 : 1) in a beaker of about 50 ml. capacity. The electrode is washed carefully with water, the solution neutralized with ammonia, and ammonium carbonate is added in slight excess. The liquid is warmed gently to facilitate settling of the precipitate, and then filtered, the precipitate being washed with 2 per cent ammonia. The filtrate is acidified with nitric acid, an excess corresponding to about 2 ml. concentrated acid being added. The solution is heated to about 80° C., and electrolysed for copper in the internal electrolysis apparatus as before, the volume of catholyte being about 200 ml.

The bismuth hydroxide precipitate is dissolved in dilute nitric acid in excess and three drops of a 50 per cent solution of hydrazine hydrate are added. The solution is diluted to about 200 ml., and electrolysed in the internal electrolysis apparatus as above at 85° to 90° C. When the amount of copper originally present is more than 30 mgm., it is advisable to test the bismuth for absence of copper.

*Example 2. Determination of Bismuth and Copper in Galena.*

To dissolve the galena it is not advisable to employ nitric acid on account of the risk of formation of lead sulphate in which some of the bismuth might become entangled. The finely crushed ore (1 or 2 gm.) is boiled for about 10 min. with 25 or 50 ml. concentrated hydrochloric acid. This is usually sufficient to decompose galena, but if the action is slow, about 1 gm. of zinc is added, and the heating continued for a few minutes. If the bismuth content is known to be very low, a larger quantity of the ore may be taken, or two 2 gm. samples, dissolved separately, may be combined for electrolysis and subsequent determination. The solution is evaporated to dryness and baked on a hot plate to remove as much free hydrochloric acid as possible. The residue is taken up with 10 ml. (1 : 1) nitric acid. Any zinc remaining from the original attack is thus dissolved, and after dilution with hot water to bring the lead chloride into solution, the liquid is filtered, and the residue washed with hot 5 per cent nitric acid. Should any appreciable residue other than siliceous matter remain, it is advisable to treat again with nitric acid, and combine the solution with the previous one. In the case of low-grade ores it may be desirable to decant off the original hydrochloric acid solution, evaporate this separately, and treat the residue with nitric acid, the two solutions being then combined.

The solution of the ore thus obtained is treated with a 2 per cent solution of potassium permanganate as above, in order to oxidize antimony to the quinquevalent state. One gram of hydroxylamine hydrochloride is added, and electrolysis for copper and bismuth is carried out exactly as described above.

**Determination of Small Quantities of Bismuth and of Copper in the Presence of Small Quantities of Silver and of Antimony, and of Large Quantities of Lead and of Tin.**

The determination of traces of bismuth and of copper in the presence of large quantities of lead and tin and also of similar impurities to those found in Miss Collin's solutions has been studied by B. L. Clarke, L. A. Wooten and C. L. Luke in the Bell Telephone Laboratories of New York

(*Industrial and Engineering Chemistry*, analytical edition, 1936, 8, 411). These workers have introduced some modifications into the method for details of which reference is made to their paper. Thus they replace the parchment thimbles by alundum shells; they remove the silver as iodide rather than as chloride, and they determine the copper in the previously weighed deposit of copper plus bismuth by iodometric titration. They also recommend that when the ratio of copper to bismuth is smaller than one, known amounts of copper should be added to the electrolyte, in order to secure better deposits. For the solution of alloys containing tin and lead in approximately equal amounts the use of nitric, hydrofluoric acid mixture is recommended.

*Example.*—Heat 10 gm. sample in a 600 ml. beaker with a mixture of 100 ml. water, 20 ml. concentrated nitric acid, and 15 ml. 48 per cent hydrofluoric acid. When solution is complete, boil for 1 min., to expel nitrous fumes, dilute to 300 ml. and cool to 40° C. Then add 1 per cent permanganate solution, until a permanent colour remains. If silver is present, remove it by precipitation with 2 ml. 1 per cent potassium iodide solution, remove any iodine by adding drop by drop freshly prepared sulphurous acid solution, digest cold for 5 to 10 min., and then filter through asbestos, wash, and dilute the filtrate to 350 ml. Into the diluted filtrate introduce two or three glass beads, and boil vigorously till colourless, and then for further 5 or 10 min. Dilute to 350 to 400 ml., colour again with permanganate, add 2 gm. tartaric acid, and, if necessary, standard copper nitrate solution (see above). After this, proceed in the ordinary manner for the determination of copper and bismuth.

**Determination of Small Quantities of Cadmium in the Presence of Large Quantities of Zinc.** (J. G. Fife, *Analyst*, 1936, 61, 681, and E. M. Collin, *Analyst*, 1930, 55, 495.)

E. M. Collin found that in order to separate traces of cadmium from much zinc by the method of internal electrolysis, the  $p_H$  of the solution should be between 4.5 and 5.5. This can be readily attained by the addition of sodium acetate

solution and a few drops of sulphuric acid, the  $p_H$  being checked by means of methyl orange, which changes colour between 4.5 and 5. A temperature of about 70° C. was recommended. Subsequent experimenters found difficulty in repeating Miss Collin's experiments—she did not state the composition of her anolyte precisely. The difficulties were traced to transfer resistances on the zinc anodes, which probably arose from the production of basic zinc salts. Satisfactory results were obtained by J. G. Fife when he used chloride solutions containing a considerable amount of ammonium chloride, in which no transfer resistances develop. It was found, however, that the concentration of the ammonium chloride must not exceed certain limits. Thus in a 20 per cent solution of the latter low results were obtained, the complexes formed evidently hindering the deposition of the cadmium. The presence of sulphates in the catholyte appears to be innocuous, thus 10 gm. Glauber's salt per 300 ml. did not affect the result.

*Example.*—The catholyte contained zinc chloride equivalent to 5 gm. zinc, 30 gm. ammonium chloride, 5 ml. 5 per cent sodium acetate solution, two drops of 2 per cent hydrochloric acid, and 0.5 ml. 50 per cent hydrazine hydrate solution (or 1 gm. hydroxylamine hydrochloride). Amount of cadmium 2 to 30 mgm. Volume of solution 300 ml. Temperature 70° C. Time 30 min. for quantities of cadmium less than 10 mgm., 45 min. for larger quantities. Anolyte: Zinc chloride equivalent to 5 gm. zinc and 10 gm. ammonium chloride in 100 ml. Anodes: Zinc foil.

For the determination of both copper and cadmium in spelter and zinc ores, the most satisfactory method appears to be to dissolve the sample in hydrochloric acid, deposit the copper and the cadmium together; weigh; redissolve in nitric acid, boil off fumes, and then deposit the copper alone in the internal electrolysis apparatus, or by means of externally generated current. The presence of the nitric acid hinders the deposition of the cadmium.

### Determination of Small Quantities of Nickel in the Presence of Large Quantities of Zinc.

The separation of nickel from zinc has already been discussed, and also the application of internal electrolysis to this separation by Hollard and Bertiaux. The method was adapted to the separation of traces of nickel by Fife (*Analyst*, 1936, **61**, 683).

*Example.*—The catholyte contained zinc chloride corresponding to 5 gm. zinc, 30 gm. ammonium chloride, 2 gm. sodium sulphite ( $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ ), about 50 ml. ammonium hydroxide ( $d = 0.88$ ). Amount of nickel 1 to 33 mgm. Volume of solution 300 ml. Temperature about  $65^\circ \text{C}$ . Temperatures above  $70^\circ$  should be avoided to prevent undue loss of ammonia. Time 30 to 45 min. Anolyte: Zinc chloride equivalent to 5 gm. zinc, 10 gm. ammonium chloride, 17 ml. ammonium hydroxide ( $d = 0.88$ ) per 100 ml. Anodes: Zinc foil.

## CHAPTER VII

### ELECTROLYTIC MICRO-ANALYSIS

Electrolytic methods lend themselves readily to gravimetric microchemistry. The small volume of liquid required greatly facilitates stirring by boiling or by externally introduced gas, and apparatus of a simpler kind than that used in macro-determinations can be employed for effecting separations by means of controlled potential.

#### Pregl's Method.

In Pregl's apparatus for copper micro-determinations the solution is maintained at boiling temperature. The electrodes are a platinum cylindrical cathode and a wire anode. Fig. 1 shows the stand with the electrolysis vessel, which is a test tube of 16 mm. external diameter and 105 mm. length. At the top is seen a vessel which is kept filled with cold water and acts as a reflux condenser, the condensed water running down the test-tube from the bent tip. The pair of electrodes is shown in fig. 2. The cathode C has a length of 30 mm. and a diameter of 10 mm. It has three glass beads of about 1.5 mm. fused on to it at the top and the bottom in order to prevent it from scraping the test-tube, when it is introduced or removed. The character of the glass must be such that it will not dissolve in the boiling electrolyte. The anode A has a total length of 130 mm. Its tip rests on the bottom of the test-tube, and is maintained in a central position in it by means of two Y-shaped glass distance pieces *d* which are shown in the figure. The tops of the cathode and anode leading-in wires are bent round to make contact by means of mercury cups provided in the arm from which the test-tube is suspended.



*Method of Working.*

The current is best obtained from two accumulators by means of the circuit shown in fig. 3. The cathode is carefully cleansed by means of hot concentrated nitric acid, alcohol and pure ether, and dried above a flame as described for macro-determinations. A hook is provided on the Pregl stand for this purpose, at the point H. Instead, a platinum hook

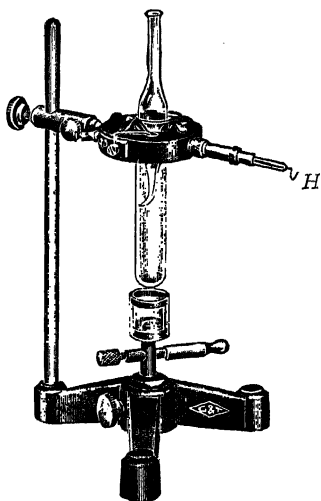


Fig. 1.—Pregl's Micro-electrical Apparatus

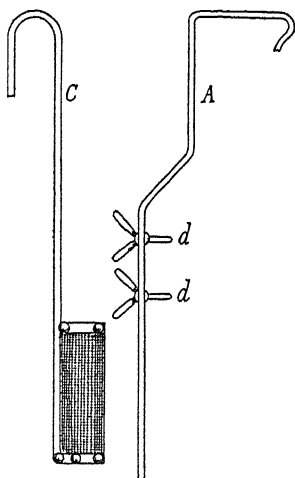


Fig. 2.—The Pair of Electrodes

fixed to a glass rod which is held in the hand may conveniently be employed. The cathode is usually hung from the pan of the micro-balance during weighing.

The surface of the liquid undergoing electrolysis should be 35 to 40 mm. above the bottom of the test-tube, and a perforated sheet of mica should be accommodated outside the test-tube and slightly above the level of the liquid, in order to protect the upper part of the stand from heat.

The potential difference is adjusted to 2 volts, the liquid

having been heated to boiling by means of the microburner shown in fig. 1. Vigorous ebullition takes place, all bumping being prevented by the oxygen which is liberated from the anode. Complete deposition may be tested for by means of ferrocyanide. It should require from 10 to 20 minutes. After the copper has been deposited the holder of the test-tube may be swung aside, and a beaker of cold water introduced from below without interfering with the current. A second beaker of cold water may be used after a few minutes. When the contents are cold, the condenser is removed, and first

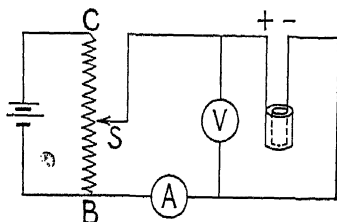


Fig. 3.—Circuit for Pregl's Method

the anode and then the cathode is carefully withdrawn. The cathode is dipped successively into distilled water, alcohol and ether, and dried over a flame as in macro-determinations. After igniting the tip of the leading-in wire which has been in contact with the mercury, and allowing the electrode to cool, it is ready for weighing on the micro-balance.

All simple depositions which can be carried out at boiling temperature may be performed in the same way with excellent results. For details regarding the determination of traces of copper in commercial products such as tinned peas, and for the determination of mercury in organic compounds, the reader is referred to Pregl's book, *Quantitative Organic Micro-analysis* (trans. by E. Fyleman), pp. 173 *et seq.*

**Method of Lindsey and Sand for Effecting Micro-deposition under Controlled Potential.** (*Analyst*, 60, 739.)

Microchemical electrolytic methods allow an auxiliary electrode to be dispensed with, when depositions are carried out under controlled potential. Owing to the small current densities required, it is possible to keep the potential difference due to ohmic resistance in the electrolyte small, provided

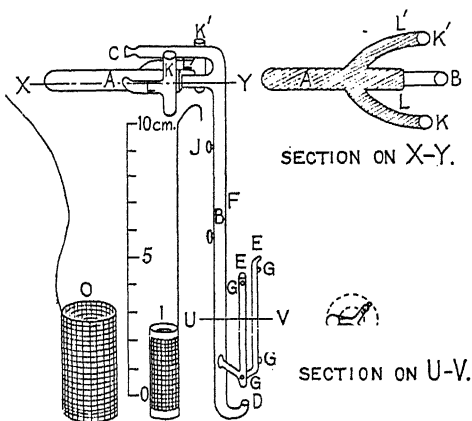


Fig. 4.—Micro-deposition under Controlled Potential: Frame and Electrodes

that a relatively large anode surrounding the cathode is employed. By this means, too, and by the use of depolarizers the variations of the anode potential may be kept within narrow limits. It thus becomes possible to control the cathode potential with considerable precision, if only the P.D. between the anode and the cathode is kept under observation, using the circuit shown in fig. 3. Cheaper voltmeters than the high-resistance instruments that are used with an auxiliary electrode may consequently be employed. Two-range instruments reading from 0 to 1.5, and 0 to 3 volts are quite suitable. If

it is desired to know the current accurately, the resistance of the voltmeter should be known so that a correction for the current flowing through it may be applied.

Gas stirring is used in order that a boiling temperature may be dispensed with without loss of efficiency. In the construction of the apparatus it was decided to incorporate a glass frame which would contain a leading-in tube for the gas, serve as a support for the outer electrode and the mercury cups, and as a cradle for the cathode. Fig. 4 shows the frame F and the electrodes O and I that were designed by Lindsey to meet these requirements. Vertical and square-on horizontal dimensions are shown to scale. The inner or working electrode I is the ordinary Pregl cathode with the beads removed. The outer electrode, the body of which is made entirely of thin gauze, is explained fully by O. It will be seen that the frame E is built upon the inlet tube B of the gas used for stirring. The entrance C is opened to a nipple, the outlet D being turned up into a capillary jet. Near the top of B is sealed a glass rod A; this is designed to be held by a boss-head on the stand, which is illustrated in fig. 5. The rod A carries two arms L and L', to which the mercury cups K and K' are attached. The arrangement of A, L, L', K and K' is shown to scale in plan on a level with the position in the view (fig. 4). Near the bottom of B the 2 mm. rods E are fitted to form a cage into which the working electrode I can be dropped, so as to sit securely, as indicated above, electrical connexion being made by means of the mercury cup K'. The outer electrode is held permanently in position by the beads G sealed on to the rods E, as shown in the figure, the connecting wire being twisted round the beads J, and dipping into the mercury cup K. The cups K and K' are permanently connected by platinum-tipped wires to the terminals T, T fitted to the stand (fig. 5). Horizontal dimensions may be taken from the sectional plan U-V. The electrolysis vessel is a test-tube ("Monax") of internal diameter 2 cm., cut to a length of about 10 cm. and holding about 12 ml. to the top of the electrodes. It rests on the bottom of a 100 ml. beaker, which serves as a water-bath, and it is held securely

in position by the frame F. The stand (fig. 5) is adapted from that of Pregl, and differs from the latter mainly in the construction of the ring support R for the beaker referred to

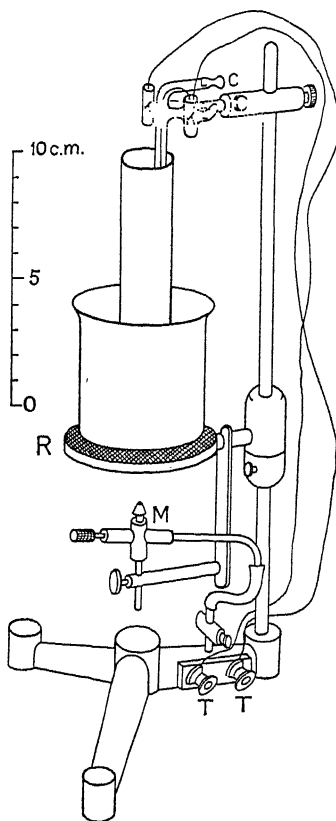


Fig. 5.—Micro-deposition: the Stand

above. The gas micro-burner M is permanently attached to R, and the assembly may be swung aside away from the beaker, which is held by hand, when it has to be lowered, in conformity with the method of working on the writer's macro-stands.

*Method of Working.*

The electrodes having been put in position, the solution is placed in the test-tube, which is raised from below until the frame touches the bottom. The water-bath is likewise raised from below, and the ring R swung into position. Water is then added until the electrodes are covered, and the gas used for stirring is admitted, its flow being adjusted by means of a screw clip near the apparatus. The gas is taken from a hydrogen, nitrogen or carbon dioxide cylinder as the case may be, and in order that no inconvenient pressure may arise, it passes through a T safety tube, the open end of which dips into a boiling tube or gas jar containing a suitable amount of water. The water bath is raised to the required temperature, the current is switched on, and the voltage between the electrodes is raised from zero to the correct value by moving the slider S (fig. 3, p. 125). This value is maintained until the metal is exhausted, the current usually falling to about one-tenth of its original value. The test-tube is then washed down with a fine jet of water, and the residual current is maintained for a few minutes. The water-bath is now removed and replaced by a beaker of cold water, current and stirring gas being left on. When the electrolyte is at room temperature, first the water-bath and then the test-tube is lowered, while the exposed parts of the inner electrode are sprayed by a jet of water until the whole has been washed. The inner electrode is then removed by a platinum hook, dipped rapidly in turn into water, alcohol and ether, or in place of the two last-named into two jars of acetone, and dried by holding it in the hot air above a bunsen flame for a few minutes, or preferably in the dryer to be described below. The tip of the leading-in wire is then heated to redness to remove traces of mercury. The electrode is allowed to cool for about a minute in the air, and is then transferred to the micro-balance, and after the lapse of fifteen minutes weighed. During this time the side doors of the balance case are kept open, whilst the large outer case in which the balance is mounted is closed. A counterpoise for the electrode is used. A convenient tool

for carrying the electrode and placing it across the hooks of the microchemical balance without handling was devised by Lindsey. It is shown in fig. 6. The technique of transferring the electrode from the platinum hook to the silver-plated tool is readily acquired.

The drying apparatus, to which reference was made above, is shown to scale in fig. 7. In this a stream of air from the hand-bellows A is blown through the tube B, which is filled with calcium chloride and cotton wool, and then the glass

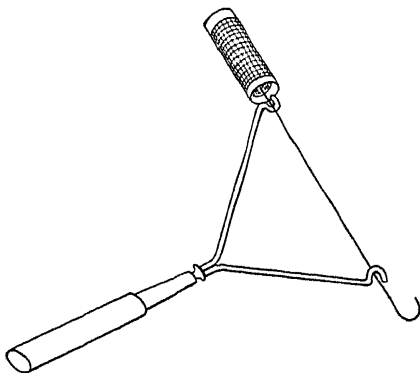


Fig. 6.—Tool for carrying Electrode

U-tube C which is heated to over  $100^{\circ}$  C. in a bath D of boiling water and glycerine. The electrode is hung in the wide limb, as shown, while the stream of warm dry air is passed over it. One minute is sufficient to dry most deposits to constant weight. When not in use, the tube is conveniently kept covered by means of a crucible lid.

Since depolarizers are usually employed with this method, a study of their effect on anode potential was made. For this purpose the writer's modified macro-electrodes were employed, the outer electrode being used as the anode. It was found that hydrazine salts were efficient under all conditions, the depolarizing efficiency of hydroxylamine salts being appreciably smaller. The latter was, however, improved by

the presence of chloride and of copper ions. The results obtained are collated in the curves shown in fig. 8. In these the P.D. between the anode and a saturated calomel electrode is plotted against the logarithm of the current density. The actual current density is also shown. The latter has been arrived at by dividing currents by the overall single surface area of the electrode employed. The electrolyte consisted of a 2.5 per cent solution of copper sulphate crystals to which

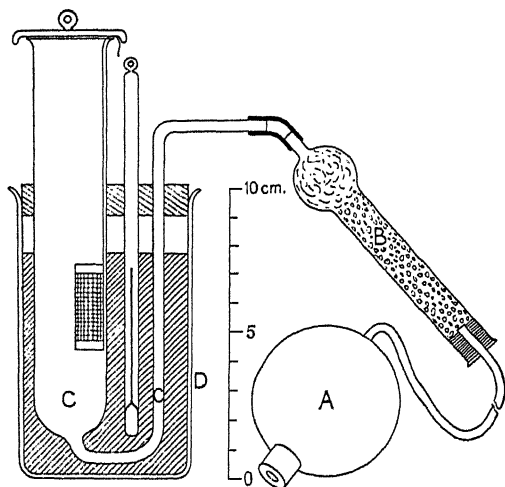


Fig. 7.—Drying Apparatus

5 ml. of  $2 \times N$  sulphuric acid and 5 ml. of depolarizer solution were added. The latter was a 2 per cent solution of either the sulphate or the hydrochloride of either hydrazine or hydroxylamine. By comparing the no-depolarizer line with that obtained with hydrazine sulphate, it can be seen that the latter reduces polarization at ordinary temperature by about 1.3 volt. The depolarizing efficiency of hydroxylamine salts is smaller, and in the absence of copper salts, smaller still. In all cases rise of temperature increases depolarizing efficiency, this being particularly marked for hydroxylamine salts at low current densities.



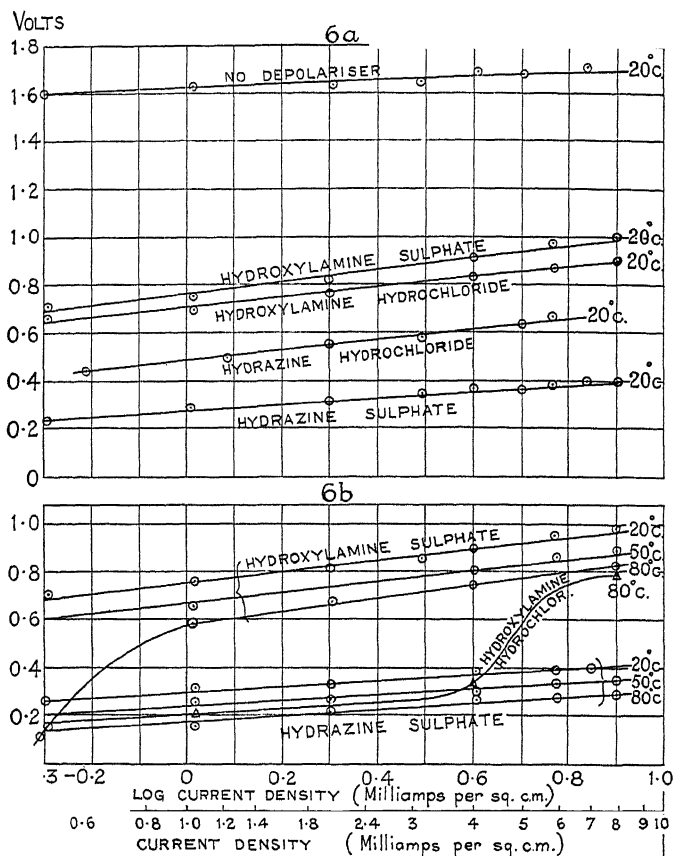


Fig. 8.—Curves showing Depolarizing Efficiencies

### Deposition and Separation of Individual Metals.

*Determination and Separation of Bismuth and Lead.*—The solutions employed in microchemical analysis are in general of the same composition as regards conductivity salts, depolarizers, &c., as those used on the macro-scale. The maximum amount of metal determined may be taken as about

6 mgm. As an example, we give the separation and determination of bismuth and lead carried out by Lindsey by the method of Lindsey and Sand (*Analyst*, 1935, 60, 744).

*Example.*—To the solution, containing not more than 6 mgm. of each metal, are added 1 ml. of nitric acid ( $d = 1.42$ ) and two drops of hydrazine hydrate solution (50 per cent). The volume is made up to 12 or 13 ml., and the solution is electrolysed at  $60^{\circ}$  to  $70^{\circ}$  C., with nitrogen stirring. The anode-cathode potential is kept at 0.8 volt, and the current falls during electrolysis from an initial value of about 70 milliamperes to about 10 milliamperes. After 10 min. from the start the tube is washed down and the electrolysis is continued at an anode-cathode potential of 0.9 volt for another 2 min., when the hot water-bath is replaced by a cold one. With the current still on, the test-tube is rapidly replaced by a shorter one containing about 12 or 14 ml. of distilled water. The cathode is then removed, and after being dipped into alcohol and ether is dried in the Lindsey dryer, and weighed.

The solution from which the bismuth has been removed is transferred to a 50 ml. tall-form beaker, some of the water which has been used for washing the electrodes being used to effect complete transference. Fifty per cent sodium hydroxide solution is added, drop by drop, until the precipitate redissolves, after which a few (10 to 20) mgm. of sodium peroxide are added, and the covered beaker is heated until no more oxygen evolution is apparent. The whole is neutralized with concentrated nitric acid, and an excess of 4 ml. is added. Finally, the remainder of the washing-water is transferred. The volume should be kept below 30 or 35 ml. The solution is electrolysed in the beaker at a temperature just below boiling-point, with nitrogen stirring and an anode-cathode P.D. of 1.2 volt, or more, the inner electrode being the anode. The current may be as great as 300 milliamperes. No water-bath is used, the beaker being heated directly by means of the micro-burner. After 12 min. the beaker is washed down, and in a further 3 min. deposition is complete. If at this stage, however, the electrode is weighed, the result is always found to be high, owing, no doubt, to sodium salts occluded by the dioxide. Accordingly an electrolysis test-tube containing 2 ml. of nitric acid and 12 ml. of water is placed in the position occupied by the beaker, and the current is reversed to redissolve the

dioxide. When the centre electrode is free from deposit, the current is reversed again, and the lead deposited as described earlier. The results are usually within 1 per cent of the theoretical amount.

### *Historical.*

The first application of micro-chemical methods to electrolytic analysis appears to have been made by E. Jänecke in 1904. He determined mercury by deposition on a gold-wire cathode of about 25 mgm. weight, a Nernst quartz-fibre balance being used.

Below we give references to papers dealing with micro-chemical electrolytic analysis. We arrange them as follows:

- (a) *Apparatus*: Nos. 2, 4, 5, 12, 13, 14, 15, 16, 20, 22, 23, 28.
  - (b) *Gold*: Nos. 6, 29.
  - (c) *Silver*: Nos. 2, 5, 8, 19.
  - (d) *Mercury*: Nos. 1, 5, 9, 19, 21, 29, 33.
  - (e) *Copper*: Nos. 2, 3, 5, 10, 11, 12, 16, 25, 29, 30, 32.
  - (f) *Bismuth*: No. 24.
  - (g) *Antimony*: No. 2.
  - (h) *Arsenic*: No. 34.
  - (i) *Lead and Tin*: Nos. 22, 24, 26, 27, 31.
  - (j) *Cadmium*: No. 19.
  - (k) *Zinc*: Nos. 8, 32.
  - (l) *Nickel and Cobalt*: Nos. 17, 18.
  - (m) *Separations by controlled potential*: Nos. 5, 23, 24, 25, 34, 35.
  - (n) *Alloys*: Nos. 7, 32.
  - (o) *Electrochemical equivalents*: No. 2.
- (1) E. Jänecke, *Z. anal. Chem.*, 1904, **43**, 547.
  - (2) O. Brill and C. B. Evans, *Trans. Chem. Soc.*, 1908, **93**, 1442.
  - (3) F. Emich and J. Donau, *Monatshefte*, 1909, **30**, 755.
  - (4) R. Heinze, *Z. angew. Chem.*, 1914, **27**, 237.
  - (5) E. H. Riesenfeld and H. F. Möller, *Z. Elektrochem.*, 1915, **21**, 137.

- (6) K. Fuchs, *Mikrochem.*, 1923, **1**, 86.
- (7) A. B. Pichler, *Z. anal. Chem.*, 1923, **68**, 321.
- (8) K. Neumann-Spullart, *Mikrochem.*, 1924, **2**, 157.
- (9) A. Verdino, *Mikrochem.*, 1928, **6**, 5.
- (10) J. W. Springer, *Z. Unters. Lebensmitteln*, 1929, **58**, 651.
- (11) E. Phillipi and F. Hernler, *Mikrochem.*, 1930; *Emich Festschrift*, 241.
- (12) C. Zbinden, *Bull. Soc. Chim. Biol.*, 1931, **13**, 35.
- (13) and (14) B. L. Clarke and H. W. Hermance, *J. Amer. Chem. Soc.*, 1932, **54**, 877, and *Mikrochem.*, 1936, **20**, 126.
- (15) E. Reichel, *Z. anal. Chem.*, 1932, **89**, 173.
- (16) to (20) A. Okáč, *Z. anal. Chem.*, 1932, **88**, 108, 189, 431; and *ibid.* 1932, **89**, 106, and *Mikrochem.*, 1932, **12**, 205.
- (21) F. Patat, *Mikrochem.*, 1932, **11**, 16.
- (22) H. Brantner and F. Hecht, *Mikrochem.*, 1933, **14**, 27 and 30.
- (23) A. J. Lindsey and H. J. S. Sand, *Analyst*, 1935, **60**, 739.
- (24) and (25) A. J. Lindsey, *Analyst*, 1935, **60**, 744, and *ibid.* 1938, **63**, 159.
- (26) M. Randall and M. S. Sarquis, *Ind. Eng. Chem. (Anal.)*, 1935, **7**, 2.
- (27) S. Wehrli, *Helv. Chim. Acta*, 1935, **18**, 546.
- (28) and (29) F. Hernler and R. Pfenigberger, *Mikrochem.*, 1936; *Molisch Festschrift*, 218, and *ibid.* 1936, **21**, 116.
- (30) H. Möhler and F. Hartnagel, *Mitt. Lebensm Hyg.*, 1936, **27**, 131.
- (31) H. Müller, *Z. anal. Chem.*, 1938, **113**, 161.
- (32) E. I. Nikitina, *Zavod. Lab.*, 1938, **7**, 162.
- (33) A. Stock, N. Neuenschwander and N. Lemmer, *Ber.*, 1938, **71B**, 550.
- (34) S. Torrance, *Analyst*, 1939, **64**, 263.

## CHAPTER VIII

### THE DETECTION AND APPROXIMATE ESTIMATION OF ARSENIC, ANTIMONY AND GERMANIUM BY ELECTROLYTIC REDUCTION TO THEIR HYDRIDES (ELECTROLYTIC MARSH TESTS)

#### Arsenic.

The employment of electrolytically generated hydrogen in the Marsh test was first attempted by C. L. Bloxam in 1861 (*Quart. Jour. Chem. Soc.*, 1861, 13, 12 and 338). In 1902 S. R. Trotman described an electrolytic Marsh test for brewing materials (*Brewers' Journal*, 1902, 445, and *J.S.C.I.*, 1904, 23, 177), and the same matter was investigated by T. E. Thorpe in 1903 (*Trans. Chem. Soc.*, 1903, 83, 974). The importance of overpotential in the electrolytic Marsh test was first pointed out by the writer. Thus Thorpe, who employed a platinum cathode, found it necessary to reduce his quinquevalent arsenic compounds to the trivalent state, whereas Trotman, who on the writer's suggestion added zinc sulphate to his solution—thus obtaining a zinc coating on his platinum cathode—was able to reduce compounds also from the quinquevalent state. An investigation of the reducing efficiency of various metals in the Marsh test in relation to their hydrogen overpotential, was carried out by Hackford on the writer's suggestion (H. J. S. Sand and J. E. Hackford, *Trans. Chem. Soc.*, 1904, 85, 1018). As a result of this, the use of lead as a material both for the cathode and the anode was recommended, and an apparatus was constructed by Hackford in which brewing materials could be examined without further treatment. In agreement with

Bloxam's experience Hackford found that mercury in spite of its high overpotential was usually quite inefficient as a cathode, and the same applied to amalgamated lead electrodes. Other experimenters have met with similar difficulties. About the time of Hackford's experiments, and in agreement with them, W. Thomson found that an electrolytic Marsh apparatus in which he employed a zinc cathode gave better results than apparatus with a platinum cathode (*Memoirs Manchester Lit. and Phil. Soc.*, 1904, No. 17).

In contrast to previous investigators, Ramberg (*Lunds. Univ. Arskrift*, N.F. (2) 14, No. 21) found mercury to be the most suitable metal for the cathode in the electrolytic reduction of arsenic acid to arsine. It is obvious that this metal has the great advantage that the physical condition of its surface is constant, and its use has now been adopted in the Government laboratory (Aumonier, *J.S.C.I.*, 1927, 46, 341). The difficulties which may arise when instructions are not rigidly adhered to will be discussed below. The effect of arsine production on the overvoltage of various cathodes was studied by W. V. Lloyd on the writer's suggestion (*Trans. Faraday Soc.*, 1930, 26, 15, and 1931, 27, 89). It was found that a cathode of metallic arsenic when subjected to high-current densities in sulphuric, oxalic, tartaric or hydrochloric acid passes from an "inactive" to an "active" condition. In the latter, it enters into combination with a considerable fraction of the hydrogen generated, and at the same time suffers a very noticeable diminution of overpotential, say from 0.62 to 0.49 volt, measured by the commutator method, (see Vol. I). The highest efficiency of 60 per cent in arsine production from electrolytic hydrogen was obtained in four  $\times$  normal hydrochloric acid solution by subjecting the electrode to the rapid alternation of a cathodic and an anodic current density of 525 and 44 milliamperes per square centimetre respectively. The reduction of arsenic acid on lead, tin and mercury cathodes was also studied. The last-named proved the most efficient. It was found that arsine production on a mercury cathode always produced a diminution of overpotential, as measured by the commutator method, showing

itself as a gradual decrease from about 0.92 to 0.45 volt during the time that the arsenic solution flowed over the cathode. Lloyd points out that the minimum value of 0.45 volt is about the same as that at which hydrogen is ordinarily liberated from an arsenic cathode. It was, however, impossible to detect any arsenic in the mercury. The inference was drawn that small although unrecognizable quantities of arsenic are deposited on the mercury cathode, and immediately converted into arsine. In other experiments it was found that the presence of zinc in the mercury inhibited this decrease of overpotential and at the same time improved the yield of arsine. Thus using an electrolytically prepared 1 per cent zinc amalgam in place of pure mercury, the yield of arsine under given conditions was increased from 32 per cent to 74.5 per cent. The inference would be that the presence of the zinc hinders any intermediate deposition of elemental arsenic.

On the writer's suggestion, the use of zinc amalgam in place of mercury in the electrolytic Marsh was then studied by J. A. Low, and it was found that the amalgam offers very distinct advantages over the pure mercury. The principal result of Low's investigation was the following. Unless necessary precautions are taken, mercury cathodes are apt to lead to trouble in the electrolytic Marsh, as small quantities of mercury frequently find their way into the solution as mercury salts. In fact, where mercury cathodes are left in contact with sulphuric acid, deposits of mercurous sulphate frequently become visible (and when this is the case, the Marsh test invariably fails). Undoubtedly mercury salts render the liquid useless for the Marsh test, since they interact with arsine, and thus remove it from the test. The formation of mercury salts on a zinc amalgam electrode does not, however, take place, since the zinc protects the mercury by going into solution in preference to it. Whether the zinc also offers advantages for the reasons surmised by Lloyd it is at present impossible to say. It is certain that oxidizing substances must be kept away from the solutions undergoing examination with the mercury cathode, as such oxidizers

would promote the formation of mercury salts. We think it desirable also to draw attention to the role of chlorides in promoting the deposition of elemental arsenic from arsenious compounds, as explained on p. 68. Such arsenic could certainly not be recovered as arsine, if actually dissolved by mercury, and even if deposited on solid cathodes, it might cause difficulty. We conclude, therefore, that when mercury cathodes are employed, arsenic should preferably be present in the quinquevalent condition, that all oxidizers must be absent, and that it is probably in all cases desirable to deposit about

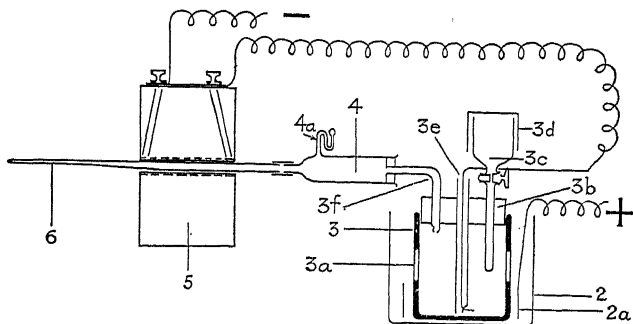


Fig. 1.—Aumonier's Apparatus for Arsenic

1 per cent of zinc from a sulphate solution into the mercury. While all substances which react with arsine must be rigidly excluded, the presence of small quantities of metals which are indifferent to it need cause no anxiety.

We now come to the description of Aumonier's method referred to above. The apparatus (fig. 1) comprises a water jacket, kept at about  $15^{\circ}\text{C}.$ , which is, however, not shown in the figure, the anode vessel and platinum foil anode of about 1.8 cm. width, 2 and 2a, the cathode cell 3, the drying tube 4, the electrically heated furnace 5 and the deposit tube 6. The cathode cell is a Royal Worcester porcelain porous pot of about 2 mm. wall thickness,  $4\frac{1}{2}$  cm. external diameter, and  $5\frac{1}{2}$  cm. height. The lower and upper parts of this pot, inside and out, are made impervious by impregnation with



montan wax or other suitable medium, an annulus *3a*, 1.5 cm. wide, the lower boundary of which is 1.8 cm. from the lower outside edge of the pot, being left porous. The pot is fitted with a rubber stopper, through which pass the following three units: (1) The delivery funnel *3c*, which is fused to a capillary stem, drawn out so as to permit the delivery of 14 c.c. dilute sulphuric acid in about 2 minutes. This funnel has a loosely fitting cover *3d* to protect it from dust. (2) A tube *3e* which is open at both ends, and which holds a 22 gauge platinum leading-in wire for the cathode. The wire is bent at right angles to fit excisions in the upper and lower end of the tube. (3) The delivery tube *3f* for the hydrogen. To the last-named is attached the drying tube 4 of about 1 cm. diameter and 5 cm. length, which is loosely packed before each experiment with neutral calcium chloride. The drying tube is furnished with the trap *4a* stopped with a drop of mercury in order to relieve gas pressure while the deposit tubes are being sealed.

The electric furnace *5* is constructed so that it will heat the deposit tubes to approximately 800° C. with a current of about 3 amp. It is run in series with the electrolytic cell which thus also takes a current of 3 amp.

From the instructions given on the working of the apparatus we note the following. The mercury is purified every few months by aeration at 150° C. for four hours, followed by distillation under reduced pressure in a slow stream of filtered air admitted by a fine capillary placed near to the bottom of the flask. After each half-day's work it is separated from the electrolyte and passed through perforated filter paper. We draw special attention to the fact that the instructions make it clear that the mercury is never left in contact with the electrolyte when no current is passing. The formation of mercury salts is thus avoided (see above). The electrolyte is 1 to 7 sulphuric acid (by volume). The calcium chloride of the drying tube *4* is prepared by leaving crystals in a vacuum desiccator over sulphuric acid for 17 hours. The cathode cell is rinsed with distilled water, and the internal coated surfaces are wiped with filter paper before use. The mercury is then put in until level with the lower edge of the porous band. The sulphuric

acid electrolyte, both inside and outside, just covers this band.

Before the furnace and deposit tube are connected to the apparatus and the test liquid is added, the current is passed for 30 min., the level of the acid is then reduced to that of the lower end of the funnel tube by suction through the funnel, after which about 1 c.c. of acid is forced back into the cell so as to free the capillary stem from gas bubbles. The furnace and deposit tube are now connected, and the current passed for another 5 min. Then 10 c.c. of test solution followed first by 3 and then by 1 c.c. of the acid are added, the electrolyte being now just above the upper edge of the porous band. The action is allowed to proceed for 15 min. after the last of the acid has entered the cell.

At the end of a test, made in duplicate, most of the solution is removed by suction as described, and a blank test is carried out. Blanks and tests should follow in a series unbroken by any time interval larger than a quarter of an hour. The circuit is kept closed until the apparatus is dismantled. Determinations are made by comparing deposits with standards obtained from known quantities of arsenic, and occasional control experiments with standard solutions are recommended. When not in use the cell is kept in dilute sulphuric acid.

To prepare the material for examination the removal of all organic matter and the distillation of the arsenic as chloride is recommended. After distillation, the chloride is treated with concentrated nitric acid and evaporated to dryness, then treated with water and evaporated again several times. The residue is finally taken up in dilute sulphuric acid, and is then ready for electrolysis. The arsenic is thus brought into the form of arsenic acid, and is quite free from hydrochloric and nitric acid. For further details the reader is referred to the original paper.

### **Antimony.**

As is well known, stibine is very much more unstable than arsine. In consequence, when stibine is generated electrolytically, it decomposes rapidly with the formation of metallic antimony, which in alkaline solution is deposited as such, whereas it dissolves in an acid electrolyte. In view of these facts, J. Grant has devised an electrolytic method based on stibine formation by means of which antimony in quantities

up to about 10 mgm. has been estimated (*Analyst*, 1928, 53, 626). The method consists in blowing a rapid stream of hydrogen past the cathode, with the result that contact of the stibine with the electrolyte is reduced to a minimum, and at the same time the cathode is cooled. The apparatus employed is illustrated in fig. 2. A is a porous pot of about 75 c.c.

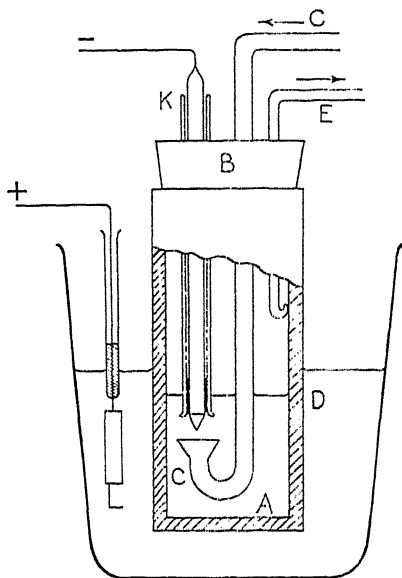


Fig. 2.—Grant's Apparatus for Antimony

capacity, with a well-fitting rubber stopper B, of which the portion inside A is well coated with paraffin wax. K is a pointed cylindrical stick, 5 mm. in diameter, of pure lead free from antimony, passing through a glass tube in the stopper, and held firmly at the bottom of the tube by a band of rubber tubing. The end of the glass tube is flared slightly, so that a gas-lock is produced in the small space between the tube, the rubber and the lead, and no liquid can splash on to the

rubber. The area of the exposed portion of the lead is 1 to 2 sq. cm. An additional seal may be made if molten paraffin wax is poured into the glass tube on top of the rubber band, between it and the lead. The hydrogen is bubbled through an alkaline solution of potassium permanganate at the rate of about two bubbles per second and directed on the cathode through C, so that the bubbles break on the point. E is an outlet tube, bent upwards at the lower end to eliminate spray, leading to a calcium chloride tube containing also a strip of lead acetate paper, and finally to the deposit tube (not shown). The porous pot stands in a beaker D, containing the platinum anode L and enough half-normal acid to reach above the level of the liquid inside. The volume of the latter was 40 c.c. The whole apparatus was immersed in a vessel containing running water. The current was about 5 amp., the P.D. across the electrodes being 10 volts.

A determination is made as follows: The lead is scraped bright, and any black deposit produced in a previous determination removed. Forty c.c. of 0.5 N hydrochloric acid are placed in the porous pot, the apparatus is swept out with hydrogen for a few minutes, the flame applied to the deposit tube, and the current switched on. Electrolysis should be continued till no further stain is obtained in the tube, and the apparatus is then free from arsenic or antimony. This step is necessary only with new apparatus. For ordinary determinations 10 c.c. of test solution of suitable concentration and 30 c.c. of 0.5 N hydrochloric acid are used.

The actual method of determination of the antimony in the deposit depends on the amount present. For 2 mgm. or more, the deposit tube should first be heated, cooled in a stream of hydrogen swept out with air, weighed, and a similar procedure followed for the determination. Amounts of from 2 to 0.01 mgm. may be dissolved in hydrochloric acid, and determined colorimetrically. Smaller amounts may be matched against standard stains, as in the Marsh test for arsenic, and it may be noted that the swift stream of hydrogen carries the stibine over to the far side of the flame before it is decomposed, and the stains are completely and sharply defined. The colorimetric method, however, is rapid and sufficiently accurate in most cases.

To carry out the latter, the deposit is dissolved in 1 c.c. concentrated hydrochloric acid, the solution diluted with 3 c.c. water, and 1 c.c. of a clear saturated aqueous solution of hydrogen sulphide. The colour is then matched in a small Nessler cylinder against that produced from a known volume of a dilute standard solution of tartar emetic (1 c.c. = 1 mgm. Sb) in 10 per cent hydrochloric acid. By these means it was possible to detect 0.001 mgm. antimony, and to determine 0.002 mgm. An accuracy of 0.001 mgm. is obtainable for quantities of 0.001 to 0.02 mgm., but for amounts above 0.05 mgm. it decreases. Within reasonable limits the colour is unaffected by the amount of acid used. When necessary, the acid solution may be diluted to a known volume, and an aliquot portion taken by means of a pipette. The conditions are rendered more comparable if the matching is carried out in the cold.

For further details reference is made to Grant's paper. Results are therein given for analyses of a number of substances containing antimony, such as Babbitt metal, rubber, lead bullion, zinc concentrate, &c. As regards the time required for a deposition, for a quantity of antimony less than  $\frac{1}{4}$  mgm. 15 min. were sufficient; for quantities up to  $\frac{1}{2}$  mgm., 20 min. sufficed, the cathode area being 1 sq. cm. and the current strength 3 amp. in both cases. With quantities from  $\frac{1}{2}$  to 7 mgm., 4 amp. were used for 30 min., and for quantities from 7 to 10 mgm., 5 amp. for 15 min.

When arsenic is present, and the determination is made gravimetrically, the combined metals are first weighed, the arsenic is then removed in a fresh solution of calcium hypochlorite (chlorite free), and the remaining antimony then weighed again. When the antimony is determined colorimetrically after dissolving in concentrated hydrochloric acid, the arsenic does not interfere, since the traces that dissolve in the acid have no appreciable influence on the colour test.

### Germanium.

Electrolytic formation of germanine is characterized by the fact that it takes place readily in alkaline solution. This makes it possible to detect small quantities of germanium in the presence of large quantities of arsenic, for alkaline arsenate solutions are not reduced electrolytically. At the writer's suggestion a method was elaborated by S. A. Coase for

estimating traces of germanium in the presence of large quantities of arsenic (*Analyst*, 1934, **59**, 462 and 747). Thus 0.03 to 0.1 mgm.  $\text{GeO}_2$  in steps of 0.01 mgm. have been determined electrolytically in the presence of arsenic corresponding to 340 mgm. The apparatus is shown in fig. 3. The process is based on Grant's stibine method. Thus hydrogen is bubbled past the cathode, but in alkaline solution cataphoresis was found so great that Grant's porous pot had to be replaced by a bell. The cathode consists of a rod of

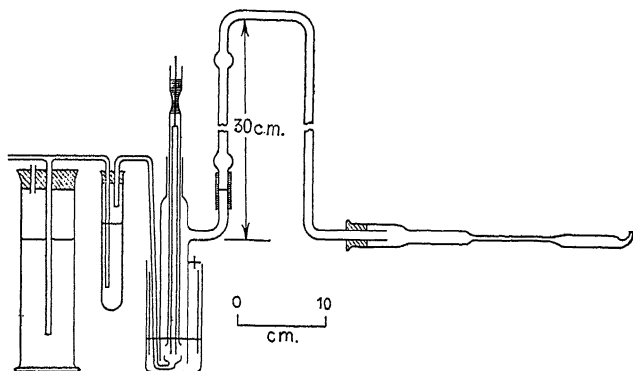


Fig. 3.—Apparatus for Germanium

nickel enclosed in a glass tube, flared at the end and provided with a small piece of rubber tubing, to form a gas lock, as in Grant's apparatus. Similarly hydrogen is bubbled past the cathode from a tube placed immediately below it. The monogermene formed is carried away to the deposit tube, where it is decomposed by heat. The hydrogen was obtained from a cylinder of the gas, passing through a safety trap and bubbler, which on test gave a satisfactory blank. The anode is a sheet of nickel, folded round against the side of the beaker. The current was obtained from the 200-volt D.C. mains with a suitable resistance. The P.D. across the apparatus was 35 volts.

The procedure was as follows: The solution to be electrolysed was placed in the beaker, and the hydrogen adjusted to about two bubbles a second. When the deposit tube, heated on the side of the constriction nearer the apparatus, had reached a dull red heat, the current was switched on. At the end of an experiment the current was switched off, and the passage of the hydrogen allowed to continue until all monogermene formed in the cathode compartment had been swept into the deposit tube. The density of the metallic stain was matched against standards previously prepared.

Other materials for the cathode than nickel were tried, but this metal alone gave satisfactory results. The circulation of the liquid in the apparatus due to gas stirring is so intense that attempts at improvement by other means led to no result. The electrolyte was a  $1\frac{1}{2}$  per cent solution of sodium hydroxide. The current employed was 5 amp., the cathode area being 1.4 sq. cm. To prevent undue heating the beaker was placed in a trough of cold water. The experiments were continued as long as the deposit increased, the times employed varying from 15 to 45 minutes.

When arsenic is present, it is oxidized to the quinquevalent state as follows: For every 0.2 gm. of arsenious oxide in 25 ml. of water 25 ml. of concentrated nitric acid are added, and the liquid is evaporated to dryness on a water-bath. For further details reference is made to the original papers.

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